SYNTHESIS OF NEW MOLYBDENUM(VI) ALKYLIDENE COMPLEXES AND RING OPENING METATHESIS POLYMERS

by

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To Min-Jung

Thoughts in Pattern

We all imagine
the way the world should be.

We all imagine
so very *well*
that we forget
to make anything
really happen
the way we imagine.

Terrell Adsit

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ABSTRACT

Chapter 1

A simple synthetic route to prepare new Mo(VI) hexafluoro-t-butoxide alkylidene complexes is described. Functionalized terminal olefins reacts with an electrophilic hexafluoro-t-butoxide neophylidene complex (Mo(NAr)(CHCMe$_2$Ph)(OR$_{F6}$)$_2$ (**1$_b$**), Ar = 2,6-i-Pr$_2$-C$_6$H$_3$, OR$_{F6}$ = OCMe(CF$_3$)$_2$) to give internal-base adducts of the type Mo(NAr)(OR$_{F6}$)$_2$(CHR') (R' = CH$_2$CH(OMe)CH$_2$CH$_3$ (**2$_b$**), CH$_2$CH(OMe)C$_6$H$_4$CH-(OMe)CH$_2$ (**3**)). The reaction of 0.5 equiv of octatetraene with **1$_b$** in a coordinating solvent such as ether or DME produced conjugated difunctional alkylidene complexes as external-base adducts ([(L)(ArN)(R$_{F6}$O)$_2$Mo=CH]$_2$(CH)$_4$, L = DME (**4**), Et$_2$O (**5**)). **5** and the THF-adduct (**6**) could also be prepared quantitatively by replacing the DME ligand with ether or THF ligands. These internal- or external-base adducts reacted with various aldehydes to give the coupled products quantitatively. They polymerized strained cyclic olefins such as methyltetracyclododecene (MTD) or 2,3-dicarbomethoxy-norbornadiene (DCMND) in high yield. Corresponding t-butoxide complexes could be generated in situ by addition of excess LiO-t-Bu to hexafluoro-t-butoxide complexes and low-polydispersity polymers were obtained in high yield. The presence of LiO-t-Bu or LiOR$_{F6}$ does not affect the polymerization reaction.

Chapter 2

A blue-light emitting electroluminescent polymer was prepared by the ring opening metathesis polymerization (ROMP) method from a norbornene type monomer (NBTPV-C5) that contains a phenylene vinylene oligomer unit as a side chain. A 50mer of NBTPV-C5 (M_w/M_n=1.10) was prepared in THF in 95% yield employing Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ as the initiator. Electroluminescent devices were made with single layers of polyNBTPV-C5, with ITO as the anode and Ca as the cathode, both by itself and in blends containing the electron transport material, biphenyl-*t*-butylphenyloxadiazole. Two layer devices using PPV (poly-*p*-phenylenevinylene) as a hole transport layer can also be prepared. Electroluminescent quantum yields of up to 0.55% have been obtained.

Chapter 3

Intramolecular photoinduced electron transfer in chromophore end-capped homopolymers and multiblock copolymers of electron donors is discussed. A series of Re chromophore, [Re(biq)(CO)$_3$(py)]$^+$, end-capped polymers was prepared from norbornene type monomers containing redox-active functional groups such as phenothiazine (PTZ) or tetramethylphenylenediamine (TMPD) by ROMP. Thus, polymers of the type Re(MTD)$_x$, Re(PTZ)$_x$, Re(TMPD)$_x$, Re(MTD)$_x$(PTZ)$_y$,

$Re(MTD)_x(TMPD)_y$, $Re(PTZ)_x(TMPD)_y$, and $Re(MTD)_x(PTZ)_y(TMPD)_z$ were prepared. These polymers showed well-behaved photoinduced intramolecular electron transfer. In the cases when the redox-inactive MTD block was interposed as a spacer block between the Re(I) chromophore and donor blocks, lifetimes of the charge separated state were increased by two orders of magnitude compared to that of chromophore-donor linked model compounds. A correlation between the electron transfer rate constants and the repeat unit numbers of an inert spacer block (MTD) was observed. However, the intramolecular forward and back electron transfer rates seemed to be limited by polymer chain dynamics rather than electron transfer energetics because of the flexibility of polymer backbones.

Chapter 4

The synthesis of polymers containing both unsaturated conjugated chains and metal nanoclusters is described. Triblock copolymers, $(MTD)_n(=CH\text{-}CH=CH\text{-}CH=)_{20}$-$(NORPHOS)_{20}$ ($\mathbf{1_n}$), n = 100, 200, 400, which contain a polyene section, a 2-exo-3-endo-bis(diphenylphosphino)bicyclo[2.2.1]heptene (NORPHOS) block and a MTD block, were prepared by ROMP. Films cast from a solution of $\mathbf{1_n}$, n = 100, 200, and Ag(hfac)(COD) (hfac = hexafluoro-acetylacetate, COD = cyclooctadiene) showed a lamella morphology while that from $\mathbf{1_{400}}$ showed an irregular pattern. The mild heat treatment (at 150°C for 13h) of these films produced silver nanoclusters (5-10 nm). The degradation of the polyene block occurred during the cluster formation, resulting in a short conjugation length of the polyene backbone. Preformed CdSe nanoclusters were doped into the cyclopolyene prepared from the diyne monomer containing diphenylphosphonyl groups by the living cyclopolymerization employing Mo(NAr)-$(CHCMe_2Ph)(OR_{F6})_2$ as the catalyst in DME. When the amount of doped clusters was less than 1%, homogeneously dispersed CdSe clusters in a polymer matrix was produced.

Chapter 5

The correlation between the rotamer interconversion rate and the structure of polymers is discussed. New molybdenum neophylidene complexes containing an unsymmetrically-substituted phenylimido ligand and phenoxide ligands, Mo(N-2-t-Bu-C_6H_4)$(CHCMe_2Ph)$(O-2-t-Bu-$C_6H_4)_2$ (**1**), Mo(2-t-Bu-C_6H_4)$(CHCMe_2Ph)$(O-2,4-t-Bu_2-$C_6H_3)_2$ (**2**) and Mo(N-2-t-Bu-C_6H_4)$(CHCMe_2Ph)$[Bipheno(t-Bu)$_4$] (**3**), Bipheno(t-Bu)$_4$ = 2,2'-[4,4',6,6'-(t-Bu)$_4$]$(C_6H_2)_2O_2$, were prepared as THF adducts from Mo(N-2-t-Bu-C_6H_4)$(CHCMe_2Ph)(OTf)_2$(DME) and the appropriate aromatic alkoxides. $\mathbf{3_{syn}}$ and $\mathbf{3_{anti}}$ were observed at low temperature and they coalesced at high temperature. The trans content of poly(NBDF6)$_{100}$ prepared employing **3** as the initiator was increased when the polymer was prepared at high temperature and prepared in toluene compared to that in THF. A series of NBDF6 100mers was synthesized at various temperature using the catalysts, Mo(N-2-t-Bu-C_6H_4)$(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**6**), Mo(NAr)$(CHCMe_2Ph)$-$(OR)_2$, R = O-2-t-Bu-C_6H_4 (**8**), $OCMe_2(CF_3)$ (**11**), $OCMe(CF_3)_2$ (**12**), and Mo(NAr)-$(CHCMe_2Ph)$[Bipheno(t-Bu)$_4$] (**10**). These polymers showed the same trend toward higher trans content of the polymer at higher temperature and in toluene.

Thesis Supervisor: Dr. Richard R. Schrock

Title: Frederick G. Keyes Professor of Chemistry

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List of Schemes

Abbreviations Used in Text

A	electron acceptor
abs	absorption
ADMET	acyclic diene metathesis
br	broad
C_α	carbon bound to metal
C_β, etc.	carbon bound to C_α, etc.
C_{ipso}	carbon in aromatic ring bound to nitrogen
C_m	carbon in the meta position in an aromatic ring
C_o	carbon in the ortho position in an aromatic ring
C_p	carbon in the para position in an aromatic ring
COD	cyclooctadiene
CS	charge separated state
CV	cyclic voltammetry
d	doublet
D	electron donor
DCMND	2,3-dicarbomethoxynorbornadiene
DME	dimethoxyethane
DPA	9,10-diphenylanthracene
EA	electron affinity
ECL	electrochemiluminescence
EL	electroluminescence
em	emission
EPDPA	ethyl (diphenylphosphonyl)dipropargylacetate
eq	equation
equiv	equivalent(s)
Et	ethyl
GPC	gel permeation chromatography
h	hours
H_α	hydrogen (proton) bound to C_α
H_β, etc.	hydrogen (proton) bound to C_β, etc.
H_m	hydrogen (proton) bound to C_m
H_o	hydrogen (proton) bound to C_o
H_p	hydrogen (proton) bound to C_p
hfac	hexafluoroacetylacetate

Hz	Hertz
IP	ionization potential
i-Pr	isopropyl
ITO	indium tin oxide
J	coupling constant in Hertz
$k_{a/s}$	rotamer interconversion rate from anti to syn
$k_{s/a}$	rotamer interconversion rate from syn to anti
K_{eq}	equilibrium constant
m	multiplet
M_n	number average molecular weight
M_w	weight average molecular weight
Me	methyl
min	minutes
MLCT	metal to ligand charge transfer
MTD	methyltetracyclododecene
NBDF6	2,3-bis(trifluoromethyl)norbornadiene
NBHole	norbornene type monomer containing 2-(N-ethyl-*m*-toluidino)ethane as a hole transport material
NBTPV-C5	norbornene type monomer containing 1,4-bis(2-(3,4,5-trimethoxyphenyl)-ethenyl)benzene as an emitter
NLO	nonlinear optical
NMR	nuclear magnetic resonance
NORPHOS	2-exo-3-endo-bis(diphenylphosphino)bicyclo[2.2.1]heptene
OTf	O_3SCF_3, triflate, trifluoromethylsulfonate
PDI	polydispersity index (M_w / M_n)
PET	photoinduced electron transfer
Ph	phenyl
PL	photoluminescence
PMMA	poly(methylmethacrylate)
PPV	poly(*p*-phenylenevinylene)
PTZ	phenothiazine
py	pyridine
q	quartet
quin	quinuclidine
ROMP	ring-opening metathesis polymerization
s	singlet

S_0	singlet ground state
S_1	first excited singlet state
sept	septet
t	triplet
t-Bu	tertiary butyl
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TLC	thin layer chromatography
TMPD	tetramethylphenylenediamine
t-PBD	biphenyl-t-butylphenyloxadiazole
UV/Vis	ultraviolet/visible
δ	chemical shift downfield from tetramethylsilane
$\lambda_{max, abs}$	wavelength of maximum optical absorption
$\lambda_{max, em}$	wavelength of maximum optical emission
$\chi^{(3)}$	third-order susceptibility
Φ	quantum yield
γ	second hyperpolarizability
τ	half-life time

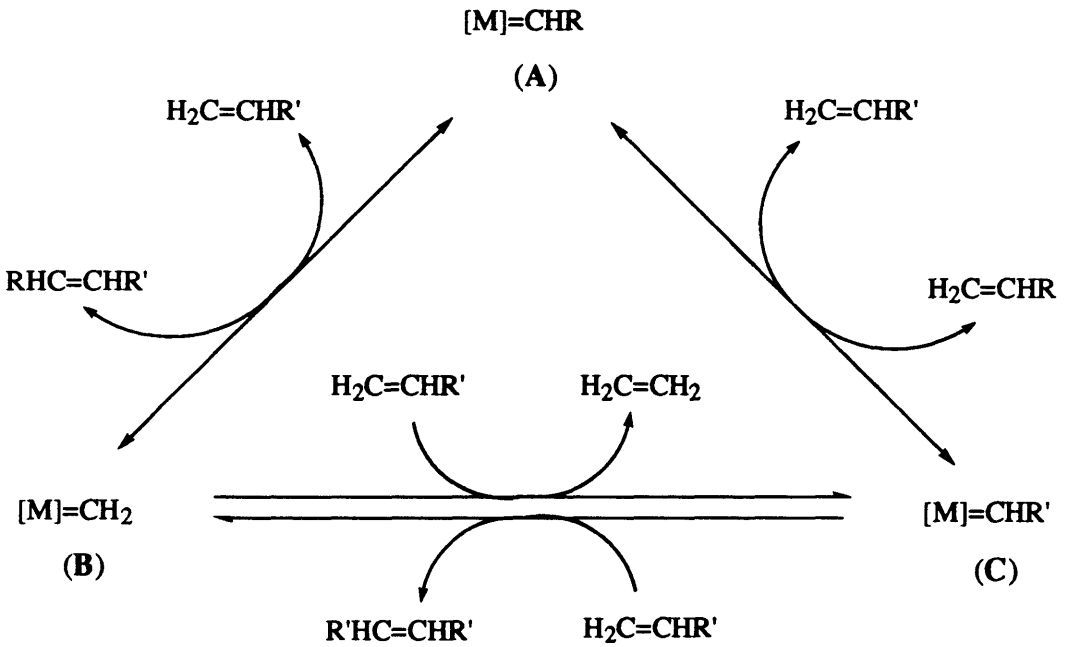
CHAPTER 1

Internal- and External-Base Adduct of New Alkylidene Complexes and Their Reactivity

INTRODUCTION

Group 6 metal alkylidene complexes of the types of M(N-2,6-*i*-Pr_2-C_6H_3)-(CHR')$(OR)_2$ (M = Mo[1,2], W[3]) were found to be effective catalysts for the metathesis of olefins and for the living ring-opening metathesis polymerization (ROMP)[4] of strained cyclic olefins. Catalytic activities of these complexes can be tuned by changing the electronic and steric nature of the ligands around the metal.[5] For example, Mo(N-2,6-*i*-Pr_2-C_6H_3)$(CHCMe_2Ph)(O$-*t*-$Bu)_2$[6] produces highly *trans* and highly tactic polymers , while Mo(N-2,6-Me_2-C_6H_3)(CHR)[(±)-BINO$(SiMe_2Ph)_2$] [7,8] generates highly *cis* and highly tactic polymers. Since the initial alkylidene ligand is introduced at the beginning of the polymer chain[6,9,10] and polymerization can be terminated in a Wittig-like capping reaction with a funtionalized benzaldehydes,[11,12] it is possible to control the nature of the group at both ends of a ROMP polymer. Such control is crucial to synthesize interesting materials such as redox-active polymers[13-15] and push-pull polyenes.[16-21] It is, therefore, important to develop routes to new alkylidene initiators for living polymerization reactions. A potential secondary benefit is that initiators other than neopentylidene or neophylidene complexes may have a lower ratio of the rate of propagation to the rate of initiation.[6,10,11,22,23] Finally, it would be desirable in some circumstances to develop a difunctional (bimetallic) initiator in order to synthesize a polymer by growing the polymer chain in two directions at the same time.[24]

The most straightforward way to prepare new mono substituted alkylidene complexes of the same basic type is via a metathesis reaction between a neopentylidene or neophylidene complexes and a terminal olefins (Scheme 1.1). Terminal alkene reacts with the original alkylidene complex (**A**), usually neopentylidene or neophylidene complexes, to generate methylidene complex (**B**) and new alkylidene complex (**C**). These new alkylidene complexes can interconvert with each other by further reacting with another alkene and all the species in this reaction are in equilibrium. In the case



Scheme 1.1. Metathesis reaction of mono substituted alkyldene complex with terminal olefins. ([M] = $M(NAr)(OR)_2$)

of simple linear alkenes such as 1-pentene with tungsten neopentylidene complexes,[25] the new alkylidene (C) was detected by NMR but could not be isolated. $Mo(NAr)(OR_{F6})_2(CHCMe_3)$ (OR_{F6} = $OCMe(CF_3)_2$) reacted with excess ethylene to give unstable metallacyclobutane complex, $Mo(NAr)(OR_{F6})_2(CH_2CH_2CH_2)$, as a major product which decomposed in solution even in the presence of PMe_3.[26] Terminal alkene metathesis using well-defined alkylidene catalyst is not well understood primarily because of instability of the intermediate methylidene complexes that are generated during the catalytic cycle. When $Mo(NAr)(OR_{F6})_2(CHCMe_3)$ is used as catalyst in acyclic diene metathesis (ADMET) polymerization,[27-35] it must be added in several portions to compensate for decomposition of (presumably) intermediate methylidene complexes. Recently, it was reported that a coordinating solvent such as DME can stabilize the molybdenum methylidene complex in solution.[36] Terminal alkenes therefore can be

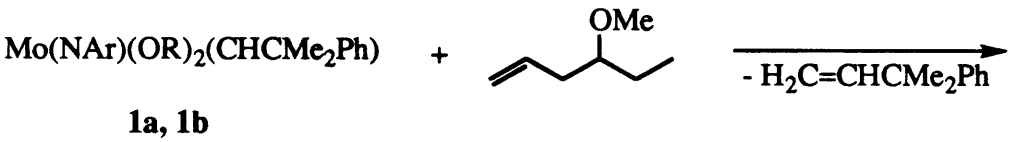
coupled in the presence of a catalytic amount of the DME adduct of the molybdenum methylidene complex ([Mo]=CH_2•DME) which is generated *in situ* from Mo(N-2,6-*i*-Pr_2-C_6H_3)(OR_{F6})$_2$(CHCMe$_2$Ph) complex and terminal alkenes.[37,38] The reaction with trialkylvinylsilane gave a stable isolable silyl substituted alkylidene complexe in good yield.[2,3] The steric protection by the substituents on the silicon and the participation of silicon-based empty d-orbital seem to be the major factors that stabilize the resulting alkylidene complex. Conjugated alkenes, such as 1,3-pentadiene,[39] ferrocene,[15] and styrene[25] can react with neopentylidene or neophylidene complexes to give isolable new alkylidene complexes as base adducts or in base-free form. The resulting alkylidene complexes are stabilized by delocalization of the partial negative charge on the α carbon into the conjugated substituent. Therefore, if a new alkylidene complex (**C**) is more stable than the original alkylidene complex (**A**) and methylidene complex (**B**), the equilibrium shifts toward **C**, which often can be isolated. In this chapter, several approaches to stabilize new alkylidene complexes by internal and external base coordination are presented and their reactivities are discussed.

RESULTS AND DISCUSSION

Intramolecular base coordination (Chelate effect)

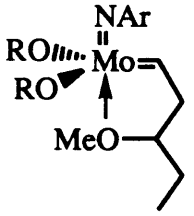
If a functional group on the alkylidene ligand can coordinate to the metal, the cyclic complex is often more stable than the acyclic one as a consequence of the so-called chelate effect. Metallacyclobutane complexes, which normally are not observable, were isolated and fully characterized if the olefins had a coordinating functional groups such as an ester or an amide.[40] A tungsten benzylidene complex also has been stabilized by internal and external oxygen base coordination.[41] In order to investigate the chelate effect in alkylidene complexes several alkenes that contain a methoxy group were prepared and their reactions with molybdenum neophylidene complexes were examined.

4-Methoxy-1-hexene, prepared from propanal in two steps, reacted with $Mo(NAr)(OR_{F3})_2(CHCMe_2Ph)$ (**1a**) in hexane to generate a new compound having an alkylidene peak (dd) at 11.94 ppm (≈ 25% conversion) when both reagents were mixed in a 1 : 1 ratio (eq 1.1). With a 10 fold excess of 4-methoxy-1-hexene, more than 80% of



1a, 1b

(1.1)



2a, 2b

NAr = N-2,6-*i*-Pr_2-C_6H_3
a; OR = $OCMe_2(CF_3)$
b; OR = $OCMe(CF_3)_2$

the new alkylidene compound was generated. Isolation of that new compound was difficult due to contamination with unreacted neophylidene complex and excess 4-methoxy-1-hexene. The more reactive $Mo(NAr)(OR_{F6})_2(CHCMe_2Ph)$ (**1b**) reacted with a slight excess of 4-methoxy-1-hexene to give orange-red $Mo[CHCH_2CH(OMe)\text{-}CH_2CH_3](NAr)(OR_{F6})_2$ (**2b**) in good yield. Five-coordinate base adducts of imido alkylidene complexes normally have the donor ligand bound in an axial position and the alkylidene and imido ligands lying in the equatorial plane.[39] Those complexes show two different isopropyl methyne (septet) resonances and four different isopropyl methyl (doublet) resonances. The NMR spectrum of **2b** (Fig 1.1) suggests that no plane of symmetry is present due to the chiral γ carbon but shows only one isopropyl methyne septet, two isopropyl methyl doublets and two slightly separated (0.11 ppm) methyl resonances for the alkoxide ligands. The structure shown in eq 1.1 (or related square-

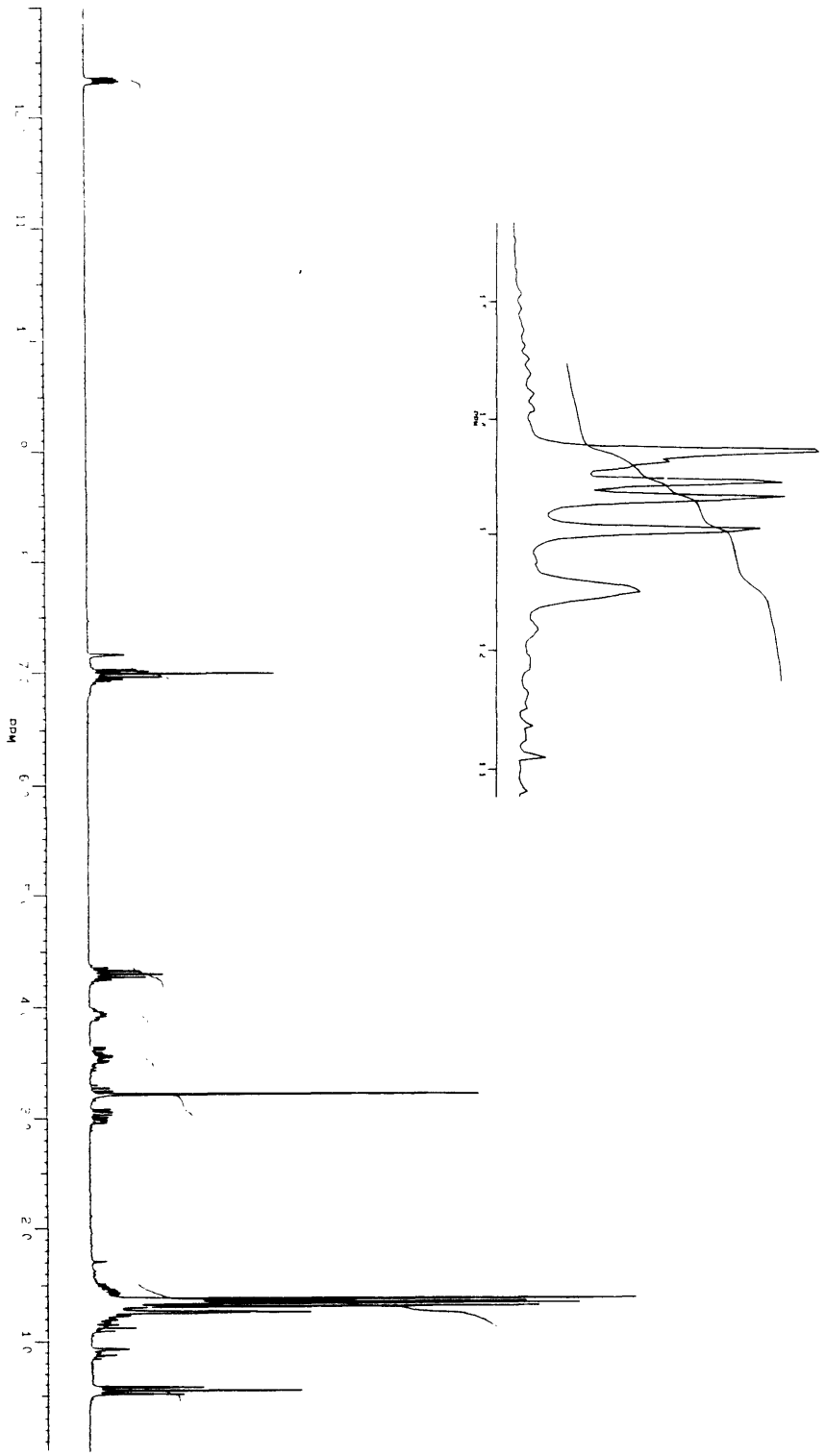
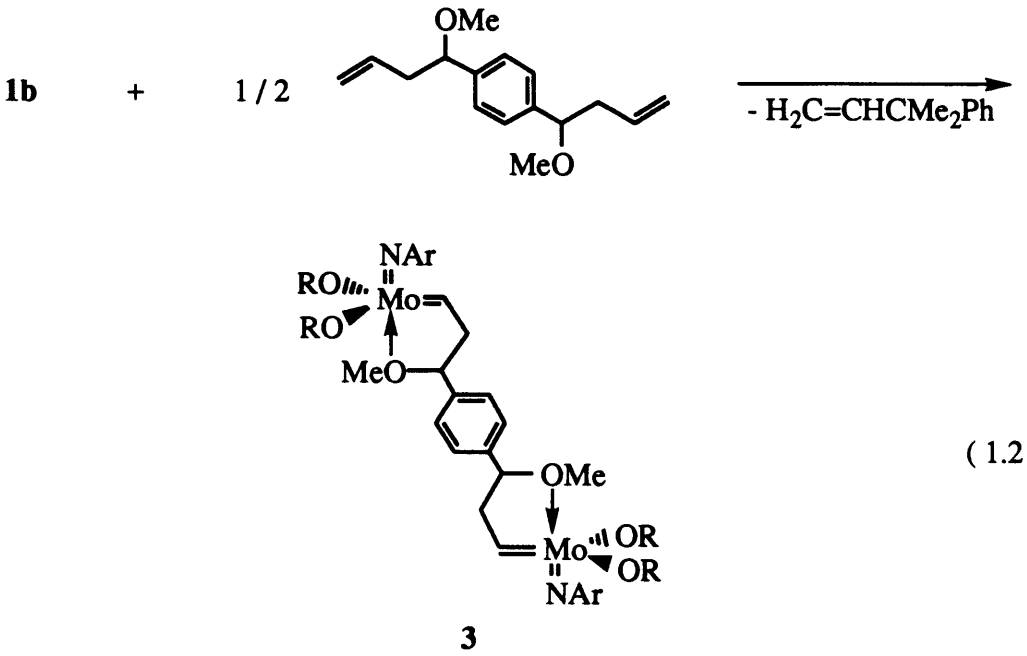


Fig. 1.1. ^{1}H NMR spectrum of $CH_3CH_2CH(OMe)CH_2CH{=}Mo(NAr)(OR_{F6})_2$ (**2b**).

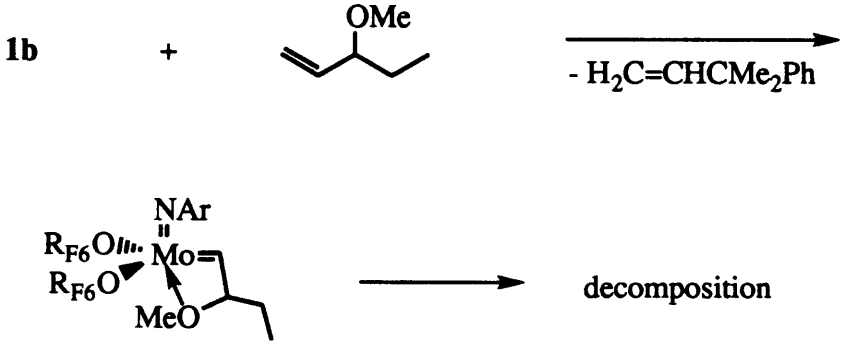
pyramidal specie containing an axial imido ligand) is consistent with these data. A related difunctional alkylidene complex (**3**; eq 1.2) was prepared in a similar manner from **1b** and the appropriate α,ω-diene in good yield. NMR data for **2b** and **3** and other



(1.2)

3

alkylidene complexes described later are summarized in Table 1. 3-Methoxy-1-pentene reacted with **1b** to generate a compound having a new alkylidene doublet peak at 12.17 ppm in up to 40% yield after 1h. The intensity of this new alkylidene peak slowly decreased with time as a consequence of decomposition, probably because the four membered chelating coordination is inadequate to stabilize the complex (eq 1.3).



(1.3)

Table 1.1. Selected ^{1}H and ^{13}C NMR data for Mo(VI) alkylidene complexes.

Alkylidene complex	$\delta(H_\alpha)$[a]	$\delta(C_\alpha)$[a]	$^{1}J_{CH}$(Hz)
Mo(NAr)(OR_{F3})$_2$($CHCMe_2Ph$) (**1a**)[b]	11.68	273.9	120
Mo(NAr)(OR_{F6})$_2$($CHCMe_2Ph$) (**1b**)[b]	12.12	284.9	121
Mo(NAr)(OR_{F6})$_2$($CHCH_2(OMe)CH_2Me$) (**2b**)	12.35	288.2	157
[($R_{F6}O$)$_2$(ArN)$MoCHCH_2CH(OMe)$]$_2C_6H_4$ (**3**)	12.38	272.2	158
(DME)($R_{F6}O$)$_2$(ArN)Mo$(CH)_6$Mo(NAr)(OR_{F6})$_2$(DME) (**4**)	12.53	267.5	127
(Et_2O)($R_{F6}O$)$_2$(ArN)Mo$(CH)_6$Mo(NAr)(OR_{F6})$_2$(Et_2O) (**5**)	12.53	267.4	132
(THF)($R_{F6}O$)$_2$(ArN)Mo$(CH)_6$Mo(NAr)(OR_{F6})$_2$(THF) (**6**)	12.41	271.5	152
(quin)(*t*-BuO)$_2$(ArN)Mo$(CH)_6$Mo(NAr)(O-*t*-Bu)$_2$(quin) (**7**)[c]	11.70	255.5	d

a) Chemical shifts reported in CD_2Cl_2 unless otherwise noted.

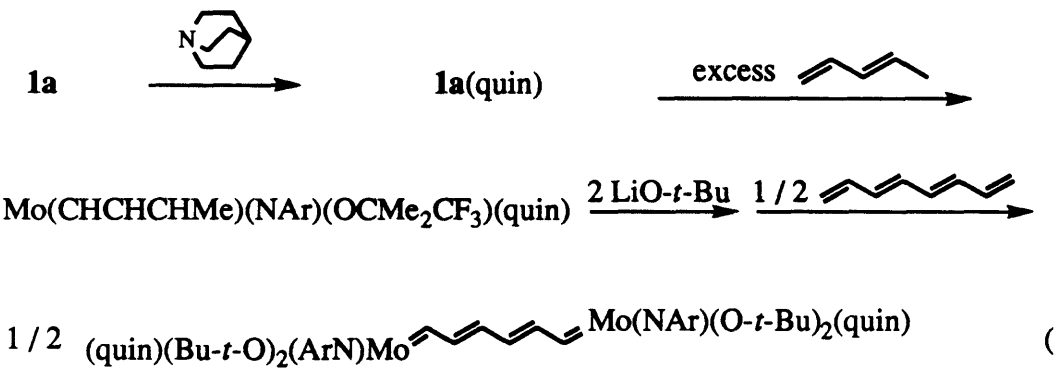
b) In C_6D_6.

c) In THF-d_8.

d) Could not be detected due to the instability of a complex.

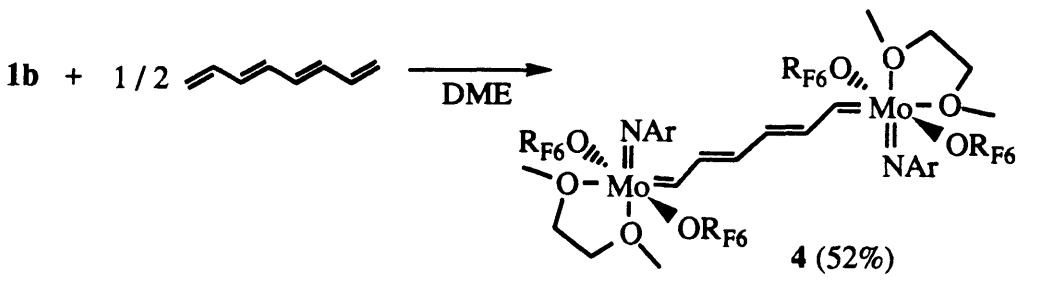
Conjugated difunctional alkylidene complexes

Conjugated difunctional alkylidene complexes of the type [(quin)(*t*-BuO)$_2$(2,6-*i*-Pr$_2$-C$_6$H$_3$N)MoCH]$_2$X (quin = quinuclidine, X = C$_6$H$_4$, C$_4$H$_4$, C$_3$H$_3$) have been prepared by Dr. Lee Y. Park from **1a** in several steps via vinyl alkylidene complexes (eq 1.4).[42]

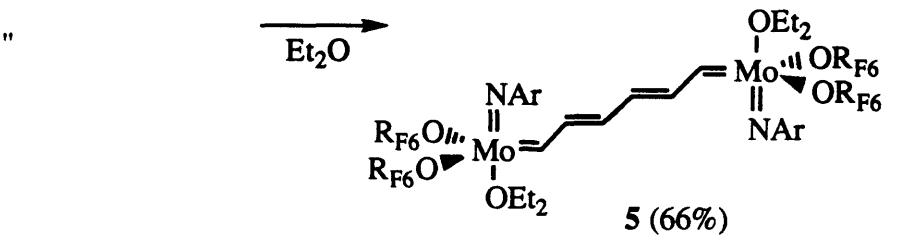


(1.4)

However, the isolated species decomposed slowly even at -35°C. Although those difunctional complexes are not very stable, they could be used as reagents to prepare polyene oligomers that have a specific length. Oxygen donor ligands appear to stabilize hexafluoro-*t*-butoxide alkylidene complexes. Therefore new synthetic routes were investigated to prepare conjugated alkylidene complexes stabilized by oxygen donor ligands, such as DME, ether or THF. DME was the most promising one perhaps because it is a bidentate base and had already been proven to stabilize electrophilic complexes such as M(NAr)$_2$Cl$_2$•DME and M(NAr)(CHR)(OTf)$_2$•DME.[1,43] The new difunctional alkylidene complex (**4**) was prepared in one step from **1b** and octatetraene. In general, **1b** was treated with 0.5 equiv of octatetraene in DME for 1h in order to yield the appropriate conjugated difunctional alkylidene complex as a base adduct (eq 1.5). The solution changed from yellow to deep red as the reaction progressed, consistent with the formation of a conjugated alkylidene complex.[39,44] The structure of **4** and **5** shown in eq 1.5 are

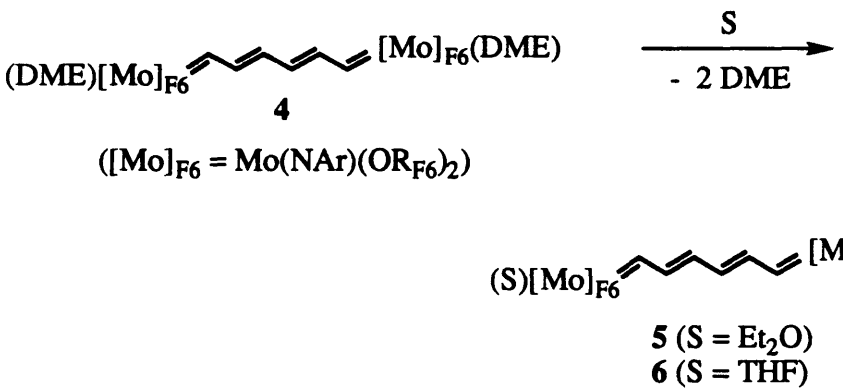


(1.5)



" THF Too slow reaction

proposed on the basis of the observed stoichiometry (Fig 1.2), and the stability of the compounds in solution and in the solid state. However, **4** must be in equilibrium in solution with free DME and a four-coordinate alkylidene complex, on the basis of the reactivity of the complex toward norbornenes and norbornadienes (see below), as well as the fact that the DME ligand in **4** can be replaced easily by ether or THF to give monoadduct **5** and **6** (eq 1.6). All three conjugated difunctional alkylidene complexes (**4**,



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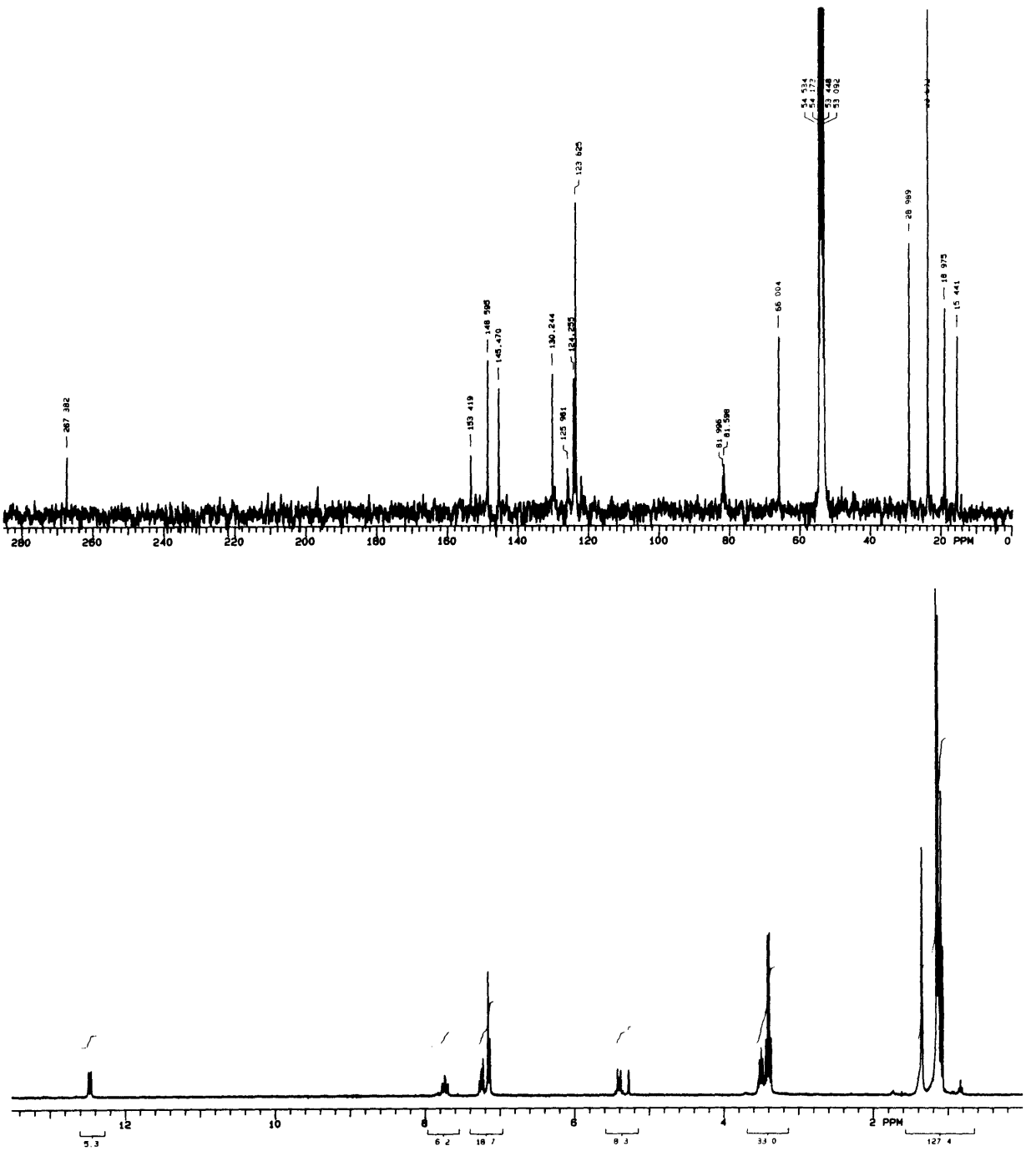
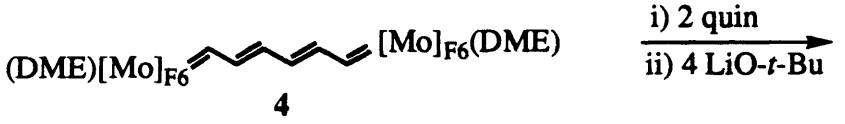


Fig. 1.2. ^{1}H and ^{13}C NMR spectra of $[(Et_2O)(ArN)(OR_{F6})_2Mo]_2(CH)_6$ (**5**).

5 and 6) are isolable, crystalline species that are stable at 25°C in solution and in the solid state. The value of $J_{CH\alpha}$ for **6** (152 Hz) is indicative of an anti orientation of the alkylidene with respect to the imido ligand, while $J_{CH\alpha}$ for **4** (132 Hz) and **5** (127 Hz) are more consistent with their being syn rotamers.

Addition of 2 equiv of quinuclidine (quin) and 4 equiv of LiO-*t*-Bu to **4** yields metallic green (quin)(*t*-BuO)$_2$(ArN)Mo(CH)$_6$Mo(NAr)(O-*t*-Bu)$_2$(quin) (**7**; eq 1.7) that



4

7

(1.7)

([Mo]$_{F0}$ = Mo(NAr)(O-*t*-Bu)$_2$)

has been prepared in a different way by Dr Lee Y. Park (eq 4). **7** is much less stable than **4** - **6** in the solid state; samples of crystalline **7** decompose even at -35°C over a period of days. It is proposed that quinuclidine is not bound strongly because of the more electron-donating nature of the *t*-butoxide ligands.

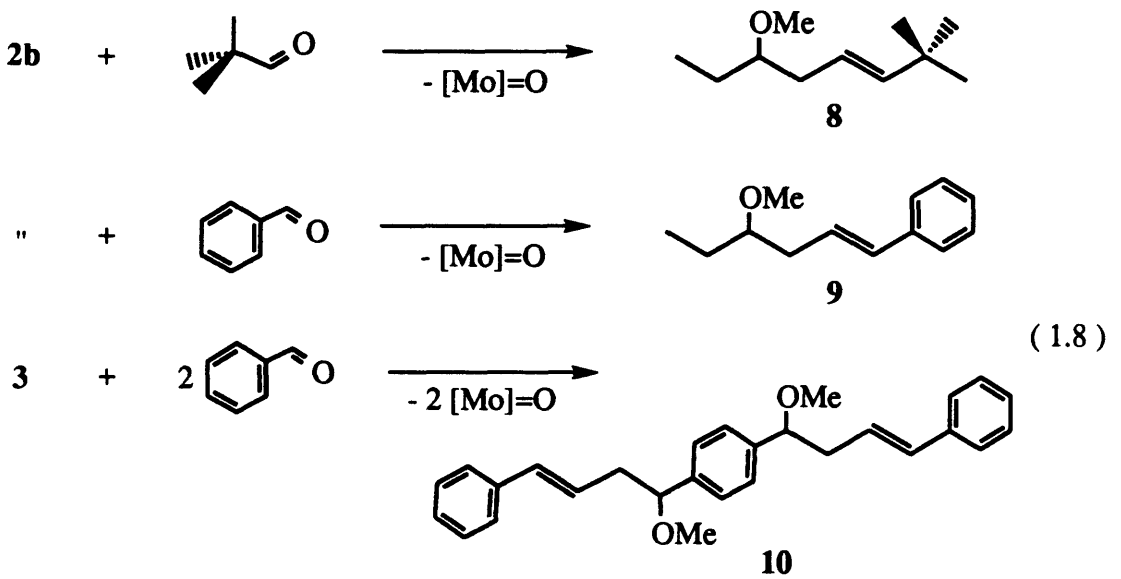
Reactions of **1b** with other conjugated terminal olefins such as hexatriene and 1,3-pentadiene in DME were very slow. Only unreacted **1b** was recovered, implying steric factors around the metal are critical in this transalkylidene metathesis reaction.

Functionalized benzylidene complexes and difunctional benzylidene complex have been prepared similarly with DME as a stabilizing base by Dr. Harold H. Fox from functionalized styrenes, styrene, 4-dimethylamino-, 2,4,6-trimethoxystyrene and divinyl-benzene.[37] He also could generate a stable methylidene complex in DME from **1b** and excess ethylene, which is active for the olefin metathesis and ADMET reactions.[38]

Reactivities of new alkylidene complexes

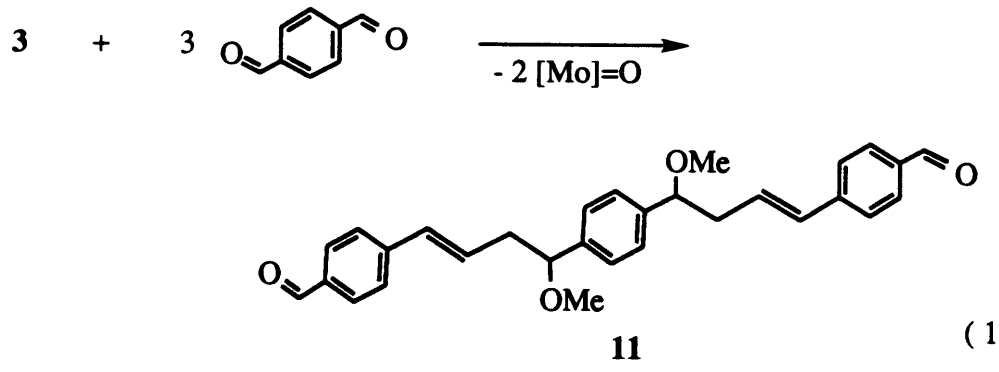
Aldehydes such as benzaldehyde or pivaldehyde react readily with alkylidene complexes of group 5, 6 and 7 metals generating metal-oxo complex and olefin quantitatively in most cases.[45] This reaction is especially useful to cap polymers prepared in living ROMP reactions.[46] A variety of substituted benzaldehydes were investigated as capping reagents in polymerizations employing Mo(VI) imido alkylidene complexes as initiators in order to explore the functionality tolerance of these compounds.[12] This Wittig-like reaction was also used to prepare the di-*t*-butyl-capped discrete length polyenes.[42] The reaction of new alkylidene complexes with benzaldehyde, pivaldehyde or terephthaldehyde was explored and the use of the resulting oligomers as soluble precursors to conjugated polymers was investigated.

Complexes **2b** and **3** react cleanly with a slight excess of benzaldehyde or pivaldehyde to afford the corresponding olefin quantitatively (eq 1.8). The reactions were complete within 1h and showed no evidence of side products. The resulting olefins are of interest as precursors to make a conjugated oligomer by elimination of methanol. Polyphenylenevinylene(PPV) has been prepared in a similar way from a soluble



(1.8)

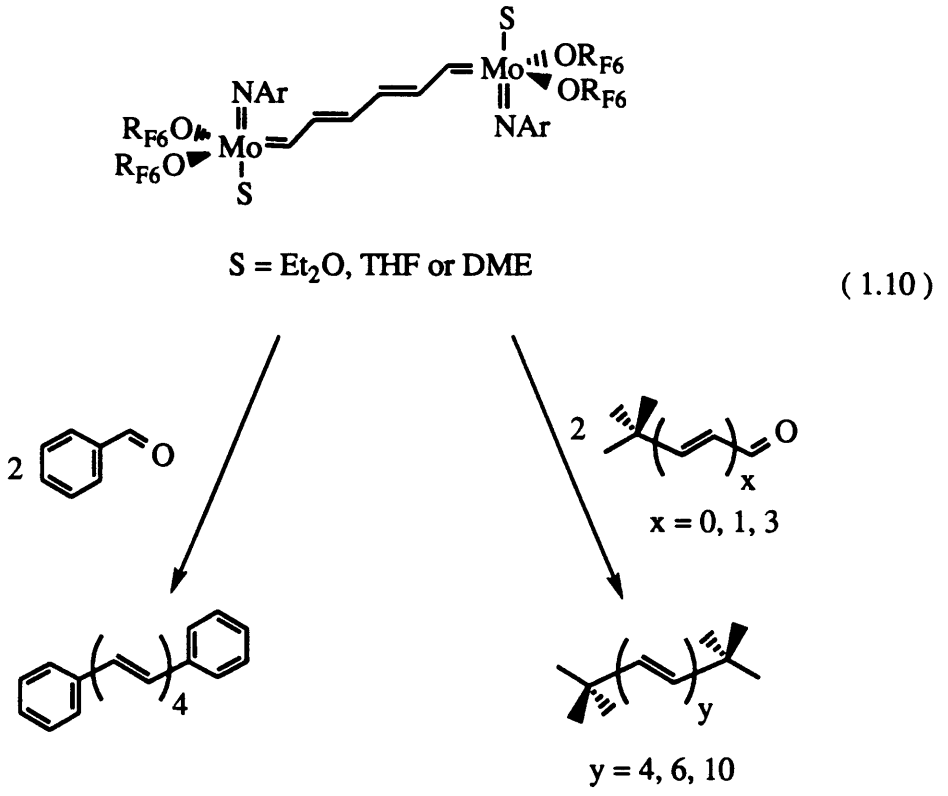
sulfonium polyelectrolytes precursor polymer followed by thermal elimination of dialkylsulfide and hydrogen halide.[47-52] Elimination of methanol from **9** and **10** by acid or base catalysis in THF solution was unsuccessful due to polymerization. Thermal elimination of methanol at 200°C generated a dark-brown residue which showed evidence of partial elimination of methanol on the basis of the red shift of UV absorption. In order to extend this method for making conjugated polymers, **3** was treated with 2,5-thiophenedialdehyde or terephthaldehyde, but this reaction generated mixtures of oligomers with different chain lengths, making it hard to analyze. When **3** reacted with 3 equiv of terephthaldehyde, the first coupled product, **11**, could be isolated in a high yield (eq 1.9). However, the thermogravimetric analysis (TGA) thermogram curve of **11** did not show any discrete degradation pattern for elimination of methanol. An apparently continuous degradation of the whole polymer was detected.



11 (1.9)

+ other higher oligomers

The conjugated bifunctional alkylidene complexes **4**, **5** and **6** react cleanly with pivaldehyde, benzaldehyde, 4,4-dimethyl-2-pentenal or 8,8-dimethyl-*trans*-2,4,6-nonatrienal in CD_2Cl_2 to afford the expected coupled products quantitatively (eq 10). These di-*t*-butyl-capped polyenes, (*t*-Bu)$(CH{=}CH)_n$(*t*-Bu) (n = 4, 6, 10), show the exactly



(1.10)

same pattern of UV and NMR spectra as the previously prepared di-*t*-butyl-capped polyenes (n = 4 - 12) did.[17,18] The relatively fast (within 1h in coordinating solvent such as THF or DME) and very clean reaction of conjugated difunctional alkylidene complexes with various aldehydes was used to prepare triblock copolymers with a short conjugated block in the middle of the polymer chain. Their photo- and electronic-properties are explored in Chapter 2.

ROMP reactions

2,3-Dicarbomethoxynorbornadiene (DCMND, 100 equiv) was polymerized smoothly in DME using **4** or **5** as the initiator. Both the monomer and the polymer are soluble in DME. The polymerization could be quenched with benzaldehyde to give a polymer in high yield with a low polydispersity (M_w / M_n; Table 1.2). The

Table 1.2. GPC and yield data for polyDCMND and polyMTD.

monomer	catalyst	solvent	M_n[a]	M_w / M_n[a]	yield(%)
DCMND(100 equiv)	**4**	DME	13,400	1.18	93
	5	DME	14,500	1.12	98
	1b	tol or THF	16,100	1.24	95
MTD(100 equiv)	**1b** + excess LiO-*t*-Bu	tol	20,400	1.03	99
MTD(200 equiv)	**3**	THF	16,800	1.35	78
	3 + excess LiO-*t*-Bu	tol	33,400	1.04	93
	4 + excess LiO-*t*-Bu	tol	43,800	1.05	94

a) Determined by GPC in THF versus polystyrene standards.

polydispersities of the polymers were larger due to a small amount of double- and half-molecular-weight polymer that was present. The half-molecular-weight polymer might arise in a reaction in which one end of the difunctional catalyst is incompletely initiated or has been terminated in some side reaction. The double-molecular-weight polymer is relatively common in polymerization reactions of this type and may arise from reactions that involve oxygen.[53]

Methyltetracyclododecene (MTD) can be polymerized using the hexafluoro-*t*-butoxide initiators. However, when polymerized in THF, polyMTD shows a relatively high polydispersity (Table II). For example, polymerization of 100 equiv of MTD by **3** in THF for 10 min followed by capping with benzaldehyde gave $(MTD)_{50}CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH(MTD)_{50}$ in 78% yield with a polydispersity of 1.35. In this case, internal coordination of the methoxy group could slow down the rate of initiation significantly relative to propagation and lead to a higher polydispersity than would otherwise be expected. An analogous reaction in which **1b** was employed as the initiator gave a polymer with a polydispersity of 1.24 after 1h of reaction. Addition of an excess of LiO-*t*-Bu (8 equiv) to a solution of **3** in toluene, followed by 200 equiv of

MTD, gave low-polydispersity polyMTD (M_w / M_n = 1.03) in 93% yield after quenching with benzaldehyde. Similar results were obtained by starting with **1b**. Although the isolation of $[(t\text{-BuO})_2(NAr)MoCHCH_2CH(OMe)]_2C_6H_4$ from the alkoxy exchange reaction was unsuccessful, probably due to the instability of the resulting complex, it could be generated *in situ* and used as a ROMP catalyst. The presence of $LiOR_{F6}$ or LiO-*t*-Bu did not seem to affect the polymerization reaction. For example, 200 equiv of MTD was added to a mixture of **4** and excess LiO-*t*-Bu in toluene without isolating the less reactive bis(*t*-butoxide) complex, and the reaction was quenched with benzaldehyde. The polymer $(PhCH)(MTD)_{100}(CH)_6(MTD)_{100}(CHPh)$ was obtained in 94% yield with a polydispersity of 1.05. The UV / Vis spectrum of this polymer is consistent with the presence of the tetraene unit.[17]

CONCLUSIONS

A variety of Mo(VI) hexafluoro-*t*-butoxide alkylidene complexes can be prepared if they are stabilized by internal or external coordination of a base. They can be employed as living ROMP catalysts and they react cleanly with a variety of aldehydes in Wittig-like reactions. A methoxy group on γ carbon in alkylidene ligand can internally coordinate to the metal and stabilize sterically less demanding alkylidene complexes that have two β hydrogens by forming a five-member ring. Internal coordination of the methoxy group appears to slow down initiation in ROMP and leads to a broader molecular weight distribution. However, these internally stabilized alkylidene complexes react cleanly with a variety of aldehydes to produce potentially interesting precursors for making conjugated oligomers with a fixed length. DME seems to be the preferred external base for stabilizing hexafluoro-*tert*-butoxide alkylidene complexes, yet the DME can easily be replaced by ether or THF and the alkylidene complexes therefore react with reactive olefins such as norbornenes and norbornadienes. When hexafluoro-*tert*-butoxide initiators are not entirely satisfactory for synthesizing low-polydispersity polymers, *t*-

butoxide initiators can be prepared in situ and employed in ROMP reactions. The presence of $LiOR_{F6}$ or LiO-*t*-Bu does not seem to affect the polymerization reaction and low-polydispersity polymers can be produced in a high yield.

The techniques described in this chapter should expand the opportunities for making polymers via living ROMP reactions and, in particular, should allow the introduction of conjugated sequences with a known, fixed length into a variety of polymers and the attachment of functional groups to both ends of a polymer. Polymers which have conjugated units with a known length for making stable and efficient electroluminescent (EL) polymers are investigated in Chapter 2, and redox-active polymers that have specific functional groups at one end of the polymer chain prepared in living ROMP method followed by Wittig-like capping reaction and photo-induced electron transfer reactions in those polymers are investigated in Chapter 3.

EXPERIMENTAL PROCEDURES

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Silica Gel (Merck grade 60, 3x40 cm) was dried (at ~130 °C) in vacuo overnight. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, benzene, and 1,2-dimethoxyethane (DME) were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane was distilled from calcium hydride under nitrogen. Toluene used for polymerization was stored over a Na/K alloy. DME and polymerization grade THF were vacuum transferred a second time from sodium benzophenone ketyl. Benzene-d_6 and CD_2Cl_2 were purged with argon and stored over molecular sieves (4Å). THF-d_8 were vacuum distilled from sodium benzophenone ketyl. HPLC grade solvents were used in GPC (gel permeation chromatography) runs and were degassed prior to use.

GPC was carried out using Shodex KF-802.5, 803, 804, 805, 800P columns, a Knauer differential refractometer, and a Viscotek Differential Refractometer / Viscometer H-500 on samples 0.1-0.3 % w / v in THF which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 - 2.75×10^6. The GPC data were analyzed using Unical 4.03 (Viscotek). UV / Vis spectra were recorded on a Hewlett-Packard 8451A Diode Array Spectrophotometer in the range of 190 nm to 820 nm. NMR data were obtained at 300 MHz (^{1}H) and 75.43 MHz (^{13}C) and are listed in parts per million downfield from tetramethylsilane. Coupling constants are listed in hertz. Spectra were obtained in benzene-d_6 at 25°C unless otherwise noted. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer.

All chemicals used were reagent grade and purified by ordinary methods. Pivaldehyde (Aldrich) was distilled and passed over alumina before use. Quinuclidine was recrystallized from diethyl ether prior to use. $Mo(NAr)_2Cl_2(DME)$,[1] $Mo(CH\text{-}CMe_2Ph)(NAr)(OTf)_2(DME)$,[2] $Mo(CHCMe_2Ph)(NAr)(OR_{F3})_2$,[1] 4, 4-Dimethyl-*trans*-2-pentenal,[54] 8, 8-dimethyl-*trans*- 2, 4, 6-nonatrienal,[42] and *trans*, *trans*-1, 3, 5, 7-octatetraene[55] were prepared by literature methods.

$Mo(CHCMe_2Ph)(NAr)(OR_{F6})_2$ (1b) . $LiOCMe(CF_3)_2$ (459 mg, 2.44 mmol) was added to a cold (-30 °C) solution of $Mo(NAr)(OTf)_2(CHCMe_2Ph)(DME)$ (0.966 g, 1.22 mmol) in 50 mL of diethyl ether. The reaction was allowed to warm to room temperature while it was stirred over a period of 1 h. The solvents were removed in vacuo and the resulting solid was extracted with pentane and the mixture was filtered. The pentane was removed in vacuo to yield a dark yellow solid. Recrystallization of the solid from pentane at -40 °C produced 802 mg (86%) of yellow crystalline product: ^{1}H NMR (C_6D_6) δ 12.12 (s, 1, Mo*CH*CMe_2Ph), 7.19-6.92 (m, 8, H_{aryl}), 3.56 (sept., 2, *CH*CMe_2), 1.53 (s, 6, O*CMe*$(CF_3)_2$), 1.18 (d, 12, CH*Me*$_2$), 1.17 (s, 6, MoCHC*Me*$_2$Ph); ^{13}C NMR (C_6D_6) δ 284.9 (d, J = 121, Mo*C*HR), 154.0 (s, C_{ipso} NAr), 148.0 (s, C_o NAr),

147.6 (s, C_{ipso} NAr), 129.6 (d, C_p NAr), 128.6 (d, C_o Ph), 126.7 (d, C_p Ph), 125.9 (d, C_m Ph), 124.2 (q, $^1J_{CF}$ = 289, OCMe(CF_3)$_2$), 124.1 (q, $^1J_{CF}$ = 289, OCMe(CF_3)$_2$), 123.5 (d, J = 159, C_m NAr), 81.3 (sept, $^3J_{CF}$ = 29, OCMe(CF_3)$_2$), 55.4 (s, MoCHCMe_2Ph), 30.4 (q, J = 133, MoCHCMe_2Ph), 28.7 (d, J = 130, CHMe$_2$), 23.8 (q, J = 127, CHMe_2), 18.8 (q, J = 130, OCMe(CF_3)$_2$). Anal. Calcd for $MoC_{30}H_{35}F_{12}NO_2$: C, 47.07; H, 4.61; N, 1.83. Found: C, 47.06; H, 4.56; N, 1.95.

$CH_3CH_2CH(OMe)CH_2CH=CH_2$. Allylmagnesium bromide (1.0 M in ether, 100 mmol) in 100 mL of ether was added to a solution of propanal (5.81 g, 100 mmol) in 200 mL of ether at 0°C over a period of 1 h. The mixture was warmed to room temperature and stirred for 1 h. A saturated aqueous solution of NH_4Cl (200 mL) was added and the organic layer was separated and dried over $MgSO_4$. 4-Hydroxy-1-hexene (5.36 g, 54%) was obtained by distilling the residue at 110°C.

4-Hydroxy-1-hexene (5.36 g, 53.5 mmol) in 20 mL of ether was added to Na (1.29 g, 53.5 mmol) suspended in 100 mL of ether. The solution was stirred for 1 h and refluxed for 2 h or until all the Na had disappeared. Dimethylsulfate (9.29 g, 73.7 mmol) was added over a period of 20 min at 25 °C and the mixture was stirred for 3 h. [NH_4]OH (5 mL, 15 N) was then added to decompose the excess dimethylsulfate. The reaction mixture was worked up with water and washed several times until the pH was neutral. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was distilled at 112 °C to give 4-methoxy-1-hexene (3.77 g, 61%): ^{1}H NMR (C_6D_6) δ 5.93-5.75 (m, 1, =CH-), 5.10-5.00 (m, 2, CH_2=), 3.12 (s, 3, OCH_3), 3.00-2.87 (m, 1, -CHOMe-), 2.30-2.07 (m, 2, =CHCH_2-), 1.50-1.38 (m, 2, -CH_2CH$_3$), 0.85 (t, 3, -CH_3).

$CH_3CH_2CH(OMe)CH_2CH=Mo(NAr)(OR_{F3})_2$ (2a). 4-Methoxy-1-hexene (4.25 μL, 29 μmol) was added to a solution of **1b** (20 mg, 29 μmol) in 1 mL of pentane. The color changed quickly from yellow to orange-red. After the mixture was stirred for 2 h, the solvent and 3-methyl-3-phenylbutene were removed in vacuo. The solid residue

was dissolved in C_6D_6 and NMR was taken: ^1H NMR (C_6D_6) δ 11.94 (dd, 1, MoCHR), 4.40 (sept, 2, $CHMe_2$), and many other peaks from **1a** and $CH_3CH_2CH(OMe)$-$CH_2CH{=}CH_2$.

$CH_3CH_2CH(OMe)CH_2CH{=}Mo(NAr)(OR_{F6})_2$ (2b). 4-Methoxy-1-hexene (47 mg, 410 μmol) was added to a solution of **1b** (0.20 g, 300 μmol) in 7 mL of pentane. The color changed quickly from yellow to orange-red. After the mixture was stirred for 2 h, the solvent and 3-methyl-3-phenylbutene were removed in vacuo. The solid product was recrystallized from ether/pentane to yield orange-red crystals (0.13 g, 66%): ^1H NMR (C_6D_6) δ 12.35 (dd, 1, Mo*CH*R), 7.12-6.90 (m, 3, H_{aryl}), 4.38-4.20 (sept, 2, *CH*Me_2), 4.00-3.87 (m, 1, -*CH*(OMe)-), 3.63-3.48 (m, 1, -CH_aH_b-), 3.20 (s, 3, O*Me*), 3.08-2.95 (m, 1, -CH_a*H*$_b$-), 1.52-1.39 (m, 2, -CH_2-), 1.36 (s, 3, OC*Me*$(CF_3)_2$), 1.35 (d, 6, CH*Me*$_2$), 1.32 (d, 6, CH*Me*$_2$), 1.25 (s, 3, OC*Me*$(CF_3)_2$), 0.54 (t, 3, -CH_3); ^{13}C NMR (CD_2Cl_2) δ 273.0 (d, J = 158, Mo*C*HR), 152.0 (s, C_{ipso}), 147.3 (s, C_o), 128.1 (d, J = 161, C_p), 124.7 (q, $^1J_{CF}$ = 293, OCMe(*C*$F_3)_2$), 124.5 (q, $^1J_{CF}$ = 293, OCMe(*C*$F_3)_2$),123.5 (d, J = 160, C_m), 83.3 (d, J = 144, -*C*H(OMe)-), 81.4 (m, O*C*Me$(CF_3)_2$), 56.3 (q, J = 137, OMe), 46.3 (t, J = 128, -CH_2-), 28.8 (d, J = 131, *C*HMe), 25.1 (q, J = 131, CH*Me*$_2$), 23.3 (q, J = 131, CH*Me*$_2$), 24.6 (t, J = 127, -CH_2-), 20.0 (q, J = 126, OC*Me*$(CF_3)_2$), 19.8 (q, J = 126, OC*Me*$(CF_3)_2$), 19.8 (q, J = 126, OC*Me*$(CF_3)_2$), 8.6 (q, J = 126, -CH_3). Anal. Calcd for $C_{26}H_{35}F_{12}NO_3Mo$: C, 42.58; H, 4.81; N, 1.91. Found: C, 42.42; H, 4.55; N, 1.97.

$CH_2{=}CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH{=}CH_2$. Allylmagnesium chloride (2.0 M, 72 mmol, 36 mL) was added dropwise to a solution of terephthaldehyde (4.02 g, 30 mmol) in 150 mL of benzene and 150 mL of THF. After the mixture was stirred for 3.5 h, it was worked up with a saturated aqueous solution of NH_4Cl at 0 °C. The organic layer was separated and washed with a saturated $NaHCO_3$ solution, rinsed twice with water, and dried over $MgSO_4$. Solvent was removed in vacuo to yield a red oily liquid (5.19 g, 74%). Colorless crystals of the dialcohol were obtained after purification by column chromatography (silica gel, THF/hexane = 1/2).

A solution of the dialcohol (1.67 g, 7.65 mmol) in 15 mL of THF was added to a suspension of NaH (0.50 g, 16.7 mmol) in 15 mL of THF. Dihydrogen was generated and the color changed to greenish-yellow upon refluxing the mixture over a period of one hour. The mixture was cooled down to 25 °C using a water bath and dimethylsulfate was added slowly. After it was stirred for 3 h, the reaction mixture was worked up as described above. The product (1.65 g, 88%) was purified by column chromatography (silica gel, Et_2O/hexane = 2/3): ^1H NMR (C_6D_6) δ 7.30 (s, 4, H_{aryl}), 5.87-5.72 (m, 2, =C*H*-), 5.10-4.98 (m, 4, CH_2=), 4.21-4.15 (dd, 2, -C*H*(OMe)-), 3.20 (s, 6, O*Me*), 2.62-2.35 (m, 4, -CH_2-); ^{13}C NMR (CD_2Cl_2) δ 141.6 (C_{ipso}), 135.5 (-*C*H=), 127.0 (C_o), 116.8 (*C*H_2=), 83.8 (-*C*H(OMe)-), 56.8 (-O*Me*), 42.8 (-*C*H_2-).

[($R_{F6}O$)$_2$(NAr)Mo=CHCH$_2$CH(OMe)]$_2$C$_6$H$_4$ (3). To a solution of **1b** (1.50 g, 2.01 mmol) in 50 mL of pentane was added CH_2=CHCH_2CH(OMe)C_6H_4CH(OMe)-CH_2CH=CH_2 (0.248 g, 1.00 mmol). After the reaction mixture was stirred for 1.5 h (the color changed from yellow to red), solvent and side products were removed in vacuo over a period of 2 h. The orange-red residue was dissolved in a minimum amount of pentane (about 15 mL) and orange crystals (0.93 g, 67%) obtained upon cooling the solution: ^1H NMR (CD_2Cl_2) δ 12.38 (dd, 2, MoC*H*R), 7.55 (s, 4, H_{aryl}), 7.20 (s, 6, imido H_{aryl}), 5.15 (dd, 2, -C*H*(OMe)-), 4.40-4.25 (m, 2, -C$H_a$$H_b$-), 4.15 (sept, 4, C*H*$Me_2$), 3.65-3.50 (m, 2, -CH$_a$*H$_b$*-), 3.35 (s, 6, -O*Me*), 1.56 (s, 6, OC*Me*$(CF_3)_2$), 1.36 (d, 12, CH*Me*$_2$), 1.33 (d, 12, CH*Me*$_2$), 1.31 (s, 6, OC*Me*$(CF_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 272.2 (d, *J* = 158, Mo*C*HR), 152.1 (s, C_{ipso} NAr), 147.4 (s, C_o NAr), 139.5 (s, C_{ipso} Ph), 128.8 (d, *J* = 159, C_o Ph), 128.3 (d, *J* = 161, C_p NAr), 124.8 (q, $^1J_{CF}$ = 286, OCMe(*C*F_3)$_2$), 124.4 (q, $^1J_{CF}$ = 286, OCMe(*C*F_3)$_2$), 123.6 (d, *J* = 158, C_m Ph), 85.3 (d, *J* = 148, -*C*H(OMe)-), 81.8 (sept, $^2J_{CF}$ = 23, O*C*Me$(CF_3)_2$), 81.2 (sept, $^2J_{CF}$ = 23, O*C*Me$(CF_3)_2$), 57.0 (q, *J* = 148, O*Me*), 49.8 (t, *J* = 131, -*C*H_2-), 28.9 (d, *J* = 130, *C*HMe_2), 25.2 and 23.3 (q, *J* = 128, CH*Me*$_2$), 20.1 (q, *J* = 132, OC*Me*$(CF_3)_2$), 20.0 (q, *J* = 132, OC*Me*$(CF_3)_2$). Anal. Calcd. for $C_{54}H_{64}F_{24}O_6N_2Mo_2$: C, 43.68; H, 4.34; N, 1.89. Found: C, 44.06; H, 4.45; N, 1.78.

$CH_3CH_2CH(OMe)CH=CH_2$. Vinylmagnesium bromide (1.0 M in THF, 100 mmol) in 100 mL of ether was added to a solution of propanal (5.81 g, 100 mmol) in 50 mL of ether at 0°C over a period of 30 min. The mixture was warmed up to room temperature and stirred for 1 h. A saturated aqueous solution of NH_4Cl (200 mL) was added and the organic layer was separated and dried over $MgSO_4$. 4-Hydroxy-1-hexene (3.15 g, 37%) was obtained by distilling the residue at 104°C.

4-Hydroxy-1-hexene (3.15 g, 36.7 mmol) in 20 mL of ether was added to NaH (80% dispersion in mineral oil, 1.32 g, 44 mmol) in 100 mL of ether. The solution was refluxed for 2 h. Dimethylsulfate (9.29 g, 73.7 mmol) was added over a period of 20 min at 25 °C and the mixture was stirred for 3 h. $[NH_4]OH$ (5 mL, 15 N) was then added to decompose the excess dimethylsulfate. The reaction mixture was worked up with water and washed several times until the pH was neutral. The organic layer was separated and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was distilled at 64°C to give 4-methoxy-1-hexene (2.06 g, 56%): ^1H NMR (C_6D_6) δ 5.65-5.50 (m, 1, =C*H*-), 5.10-4.98 (m, 2, CH_2=), 3.25 (m, 1, -C*H*OMe-), 3.14 (s, 3, -O*Me*), 1.72-1.36 (m, 2, -CH_2CH_3), 1.12 (t, 3, -CH_3).

Reaction of 1b with $CH_3CH_2CH(OMe)CH=CH_2$. A solution of CH_3CH_2CH-$(OMe)CH=CH_2$ (4.5 μL of 67% solution in Et_2O, 30 μmol) was added to a solution of **1b** (21 mg, 28 μmol) in 0.8 mL C_6D_6 and the mixture was shacked well. After 1h NMR showed new doublet alkylidene peak at 12.17 ppm. However this peak slowly decreased as time passed, and after 1 day no doublet peak was detected.

$(DME)(R_{F6}O)_2(NAr)Mo(CH)_6Mo(NAr)(OR_{F6})_2(DME)$ (4). A solution of octatetraene (7.0 mg, 66 μmol) in 1 mL of DME was added at 25 °C to a solution of **1b** (98.0 mg, 132 μmol) in 4 mL of DME . After the mixture was stirred for 1 h (color changed from yellow to dark red), solvent was removed in vacuo and the residue was dissolved in pentane. The insoluble brown powder was filtered and recrystallized from pentane/CH_2Cl_2 to yield dark-red crystals (52 mg, 52%): ^1H NMR (CD_2Cl_2) δ 12.53 (d,

2, MoC*H*R), 7.80 (m, 2, *H*β), 7.35-7.20 (m, 6, H_{aryl}), 5.50-5.40 (m, 2, H_γ), 3.62-3.48 (sept, 4, C*H*Me_2), 3.50 (s, 8, -OC*H*$_2$-), 3.35 (s, 12, -O*Me*), 1.40 (s, 12, OC*Me*$(CF_3)_2$), 1.20 (d, 24, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ 267.5 (d, *J* = 127, MoCHR), 153.4 (s, C_{ipso}), 148.6 (s, C_o), 145.5 (d, *J* = 156, C_β), 130.2 (d, *J* = 161, C_p), 124.3 (d, *J* = 135, C_γ), 123.7 (q, $^1J_{CF}$ = 247, OCMe(*C*F_3)$_2$), 123.6 (d, *J* = 160, C_m), 81.8 (sept, $^2J_{CF}$ = 20, O*C*Me$(CF_3)_2$), 72.2 (d, *J* = 145, -O*C*H_2-), 59.1 (q, *J* = 140, O*Me*), 29.0 (d, *J* = 129, *C*HMe_2), 23.6 (q, *J* = 127, CH*Me*$_2$), 19.0 (q, *J* = 132, OC*Me*$(CF_3)_2$). Anal. Calcd for $C_{54}H_{72}F_{24}N_2O_8Mo_2$: C, 42.53; H, 4.76; N, 1.84. Found: C, 42.97; H, 4.76; N, 1.77.

(Et$_2$O)(R$_{F6}$O)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(Et$_2$O) (5). This complex was prepared by two routes as described below. (a) A solution of octatetraene (7.0 mg, 66 μmol) in 1 mL of ether was added at 25 °C to a solution of **1b** (98.0 mg, 132 μmol) in 4 mL of ether. Color changed quickly to dark-red and a precipitate formed. After the mixture was stirred for 1 h, the precipitate was collected and rinsed with cold pentane to give dark-brown powder (65 mg, 66%). (b) The DME ligand in **4** was easily replaced by dissolving the compound in ether, generating the ether adduct quantitatively: ^{1}H NMR (CD_2Cl_2) δ 12.52 (d, 2, MoC*H*R), 7.80 (m, 2, Hβ), 7.35-7.10 (m, 6, H_{aryl}), 5.52-5.35 (m, 2, H_γ), 3.65-3.35 (m, 12, -C*H*Me_2 and -OC*H*$_2$-), 1.40 (s, 12, OC*Me*$(CF_3)_2$), 1.20 (d, 24, -CH*Me*$_2$), 1.15 (t, 12, OCH$_2$*Me*); ^{13}C NMR (CD_2Cl_2) δ 267.4 (d, *J* = 132, MoCHR), 153.4 (s, C_{ipso}), 148.6 (s, C_o), 145.5 (d, *J* = 157, C_β), 130.2 (d, *J* = 161, C_p), 124.3 (d, *J* = 153, C_γ), 123.8 (q, $^1J_{CF}$ = 276, OCMe$(CF_3)_2$), 123.6 (d, *J* = 161, C_m), 81.6 (sept, $^2J_{CF}$ = 32, O*C*Me$(CF_3)_2$), 66.0 (t, *J* = 146, -O*C*H_2-), 29.0 (d, *J* = 131, *C*HMe_2), 23.6 (q, *J* = 129, CH*Me*$_2$), 19.0 (q, *J* = 133 OC*Me*$(CF_3)_2$), 15.4 (q, *J* = 127, OCH$_2$*Me*).

(THF)(R$_{F6}$O)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OR$_{F6}$)$_2$(THF) (6). The DME ligand in **4** was also easily replaced by dissolving the compound in THF, generating the THF adduct quantitatively: ^{1}H NMR (CD_2Cl_2) δ 12.41 (d, 2, MoC*H*R), 7.78 (m, 2, Hβ), 7.35-7.15 (m, 6, H_{aryl}), 5.37 (m, 2, H_γ), 3.73 (m, 8, -OC*H*$_2$-), 3.63 (m, 4, C*H*Me_2), 1.79 (m, 8, -OCH$_2$C*H*$_2$-), 1.32 (s, 12, OC*Me*$(CF_3)_2$), 1.19 (d, 24, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ

271.5 (d, J = 152, Mo*C*HR), 153.1 (s, C_{ipso}), 148.5 (s, C_o), 146.4 (d, J = 156, C_β), 129.8 (d, J = 161, C_p), 124.4 (q, $^1J_{CF}$ = 283, OCMe(*C*F_3)$_2$), 124.2 (d, J = 155, C_γ), 123.6 (d, J = 162, C_m), 81.6 (sept, $^2J_{CF}$ = 29, O*C*Me(CF$_3$)$_2$), 69.3 (t, J = 147, -O*C*H$_2$-), 28.8 (d, J = 128, *C*HMe$_2$), 25.8 (t, J = 133, -OCH$_2$*C*H2-), 23.7 (q, J = 127, CH*Me*$_2$), 18.6 (q, J = 132, OC*Me*(CF$_3$)$_2$).

(quin)(Me$_3$CO)$_2$(NAr)Mo(CH)$_6$Mo(NAr)(OCMe$_3$)$_2$(quin) (7). Quinuclidine (1 mL of the stock solution of 11 mg / 5mL CH_2Cl_2, 19.8 μmol) was added to a solution of **4** (15 mg, 9.8 μmol) in 1 mL of CH_2Cl_2. The reaction mixture stirred for 10 min. A solution of LiO-*t*-Bu (1mL of the stock solution of 3.4 mg / 5 mL CH_2Cl_2, 39.2 μmol) was added and the mixture was stirred for 40 min. The solvent was removed in vacuo and the residue was extracted with pentane. A brown powder was collected and was washed with cold pentane. Although the reaction proceeded quantitatively based on the ^{1}H NMR spectrum of the crude mixture, the isolated compound was not pure owing to the instability of the product and the contamination of alkoxides: ^{1}H NMR (THF-d_8) δ 11.70 ppm (b, 2, H_α-vinyl alkylidene), 7.55 (b, 2, H_β-vinyl alkylidene), 7.10 (b, 6, H_m and H_p), 5,28 (b, 2,H_γ-vinyl alkylidene), 3.96 (b, 4, C*H*Me$_2$), 2.90 (b, 12, H_α-quin), 1.52 (b, 12, H_β-quin), 1.22 (bs, 18, C*Me*$_3$), 1.99 (bd, 12, CH*Me*$_2$). ^{13}C NMR δ 255.5 (C_α), 147 (tentatively assigned to C_β), 122.8 (tentatively assigned to C_γ). More extensive characterization of **7** has been difficult due to its thermal instability.

Reactions with aldehydes. Complexes **2b, 3, 4,** and **5** were each treated with pivaldehyde and benzaldehyde and the expected coupled products were obtained quantitatively. Complex **3** was reacted with excess terephthaldehyde in a similar procedure to give a mixture of coupled products. The general procedure was dissolving alkylidene complexes in CH_2Cl_2 or THF followed by an addition of appropriate aldehydes (in 10% excess), and removing metal oxo product by the passing through the silica gel column (ether or THF eluent).

$CH_3CH_2CH(OMe)CH_2CH=CHCMe_3$. 2b (10.0 mg, 13.6 μmol) was dissolved in 0.8 mL of C_6D_6 and slight excess of pivaldehyde (1.29 mg, 15.0 μmol) was added. The solution was shacken well and an NMR spectrum was taken after 15 min, which showed that the reaction was complete with no side reactions. The solution was passed through a column of silica gel in order to remove the metal-oxo complex. The product was collected from the Et_2O eluent: ^1H NMR (C_6D_6) δ 5.55-5.35 (m, 2, H_{vinyl}), 3.15 (s, 3, O*Me*), 2.99 (m, 1, -C*H*(OMe)-), 2.20 (m, 2, =CHCH_2-), 1.47 (m, 2, -CH_2-), 1.00 (s, 9, CMe_3), 0.92 (t, 3, CH_3).

$CH_3CH_2CH(OMe)CH_2CH=CHC_6H_5$. 2b (34.0 mg, 46.3 μmol) was reacted with benzaldehyde (4.92 mg, 46.3 μmol) in 4 mL of pentane for 1h. After the metal-oxo complex was removed by passing through a silica gel column, the expected coupled product was obtained (8.5 mg, 97%): ^1H NMR (C_6D_6) δ 7.18 (m, 1, *p*-Haryl), 7.06-6.87 (m, 4, *o*- and *m*-H_{aryl}), 6.30-6.05 (m, 2, H_{vinyl}), 3.05 (s, 3, O*Me*), 2.90 (m, 1, -C*H*(OMe)-), 2.19 (m, =CHCH_2-), 1.45 (m, 2, -CH_2-), 0.78 (t, 3, CH_3).

$Me_3CCH=CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH=CHCMe_3$. 3 (10 mg, 6.7 μmol) was treated with pivaldehyde (1.70 μL, 14.7 μmol) in 0.8 mL of C_6D_6 to give the expected coupled product quantitatively: ^1H NMR (CD_2Cl_2) δ 7.20 (s, 4, H_{aryl}), 5.40-5.18 (m, 4, H_{vinyl}), 4.09 (t, 2, -C*H*(OMe)-), 3.18 (s, 6, O*Me*), 2.25-2.40 (m, 2, -C$H_a$$H_b$-), 2.35-2.20 (m, 2, -C$H_a$$H_b$-), 0.91 (s, 18, C$Me_3$).

$C_6H_5CH=CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH=CHC_6H_5$. 3 (30.0 mg, 20.8 μmol) was reacted with benzaldehyde (4.84 mg, 45.6 μmol) in 2 mL of pentane for 1h. Coupled product (8 mg, 96%) was isolated as described above: ^1H NMR (C_6D_6) δ 7.28-6.97 (m, 14, H_{aryl}), 6.37-6.20 (m, 4, H_{vinyl}), 4.08 (m, 2, -C*H*(OMe)-), 3.08 (s, 6, O*Me*), 2.80-2.68 (m, 2, -C$H_a$$H_b$-), 2.57-2.46 (m, 2, -C$H_a$$H_b$-).

OHC-$C_6H_5CH=CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH=CHC_6H_5$-CHO. **3** (323 mg, 233 μmol) was treated with terephthaldehyde (94.0 mg, 698 μmol) in 20 mL of CH_2Cl_2 for 1h. After the solvent was removed, the residue was redissolved in benzene

and chromatographied in a silica gel column. The first eluted fraction contained excess terephthaldehyde. The solvent was then changed to pentane/Et_2O (1/1) and pale yellow solution was collected which contained product. The pale yellow solid product (68 mg, 64%) was obtained after the solvent was evaporated: ^1H NMR (CD_2Cl_2) δ 9.94 (s, 2, -C*H*O), 7.62 (dd, 8, side ring H_{aryl}), 7.33 (s, 4, centre ring H_{aryl}), 6.54-6.35 (m, 4, H_{vinyl}), 4.32-4.25 (dd, 2, -C*H*(OMe)-), 3.23 (s, 6, O*Me*), 2.80-2.55 (m, 4, -CH_2-).

H_5C_6(CH=CH)$_4C_6H_5$. **4** (10 mg, 6.6 μmol) was treated with benzaldehyde (1.5 μL, 7.3 μmol) in 0.8 mL of THF-d_8 for 2h to generate the expected coupled product quantitatively: ^1H NMR (CD_2Cl_2) δ 7.42-7.18 (m, 10, H_{aryl}), 6.96-6.84 (m, 2, H_α), 6.65-6.46 (m, 6, $H_{\beta,\gamma \text{ and } \delta}$).

(*t*-Bu)(CH=CH)$_4$(*t*-Bu). **4** or **5** (17.0 mg, 11.1 μmol) was dissolved in 0.8 mL of CD_2Cl_2 and pivaldehyde (2.70 μL, 24.4 μmol)) was added. The solution was shacken well and NMR showed that the reaction was complete after 20 min. This NMR solution was passed through a column of silica gel in order to remove the metal-oxo complex. The product was isolated as a white solid (2 mg, 83%). This compound and the previously prepared polyene were identical by NMR and UV/Vis: ^1H NMR (CD_2Cl_2) δ 6.20-5.98 (m, 6, $H_{\beta,\gamma \text{ and } \delta}$), 5.73 (d, 2, H_α), 1.04 (s, 18, C*Me*$_3$).

(*t*-Bu)(CH=CH)$_6$(*t*-Bu). **5** (33 mg, 22 mmol) was dissolved in CD_2Cl_2 and 4,4-dimethyl-*trans*--2-pentenal (6.0 μL, 44 μmol) was added. After stirring the solution for 15 min, the solvents were removed in vacuo, leaving a red solid. This material was purified by chromatography on a column of silica gel; the product was eluted with pentane. The product was isolated as a pale yellow solid (5 mg, 84%). This compound and the previously prepared polyene were identical by NMR and UV/Vis: ^1H NMR (CD_2Cl_2) δ 6.32-5.95 (m, 10, H_{vinyl}), 5.77 (d, 2, H_α), 1.03 (s, 18, C*Me*$_3$).

(*t*-Bu)(CH=CH)$_{10}$(*t*-Bu). **5** (17.0 mg, 11.4 μmol) was dissoluved in 1 mL of CD_2Cl_2 and 8, 8-dimethyl-*trans*-2, 4, 6-nonatrienal (6.0 mg, 36.5 μmol) was added. After the mixture was stirred for 15 min, an orange-red precipitate was formed. The

solvent was removed in vacuo and the residue was extracted with pentane and CH_2Cl_2 to give a red solid (4mg, 94%). This solid product is slightly soluble in THF and could be characterized only by UV which matched well with the reported value.[17]

$(DCMND)_{50}(CH)_6(DCMND)_{50}$. **5** (10 mg, 6.7 μmol) was dissolved in 4 mL of DME. The monomer (140 mg, 671 μmol) was dissolved in 1 mL of DME and added all at once to a stirred solution containing the catalyst. After 90 min, 5.4 μL of benzaldehyde was added to terminate the reaction. The polymer was precipitated in methanol and dried in vacuo to give 137 mg of polymer (98%). Polymerizations involving the other catalysts were conducted under similar conditions.

$(MTD)_{100}CHCH_2CH(OMe)C_6H_4CH(OMe)CH_2CH(MTD)_{100}$. LiO-*t*-Bu (5.0 mg, 54 μmol, 100% excess) was added to the solution of **3** (10 mg, 6.7 μmol) in 5 mL of toluene and the mixture was stirred for 1 h. 200 Equiv of MTD (234 mg, 1.34 mmol) were added all at once, and after 10 min the reaction mixture was capped with benzaldehyde (reaction time 1 h). The polymer was precipitated in 100 mL of methanol and dried in vacuo to yield 219 mg (93%) with a polydispersity of 1.04.

$(MTD)_{100}(CH)_6(MTD)_{100}$. The same procedure was used as described above to make this polymer using **4** or **5** as a catalyst. A white polymer was obtained, which had a polydispersity of 1.05 (94% yield).

REFERNCES

(1) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.

(2) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(3) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262.

(4) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.

(5) Feldman, J.; DePue, R. T.; Schaverien, C. J.; Davis, W. M.; Schrock, R. R. in "Advances in Metal Carbene Chemistry"; U. Schubert, Ed.; Kluwer: Boston, 1989; pp 323.

(6) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

(7) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.

(8) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.

(9) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(10) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495.

(11) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062.

(12) Mitchell, J. P.; Gibson, V. C.; Schrock, R. R. *Macromolecules* **1991**, *23*, 1220.

(13) Fox, M. A. *Acc. Chem. Res.* **1992**, *25*, 569.

(14) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363.

(15) Albagli, D.; Bazan, G. C.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150.

(16) Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763.

(17) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

(18) Park, L. Y.; Stieglitz, S. G.; Crowe, W. M.; Schrock, R. R. *Macromolecules* **1991**, *24*, 3489.

(19) Williams, D. J. *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 690.

(20) Barzoukas, M.; Blanchard-Desce, M.; Josse, D.; Lehn, J.-M.; Zyss, J. *Chem. Physics* **1989**, *133*, 323.

(21) Chemla, D. S.; Zyss, J. ; Academic Press: Boston, MA, 1987; Vol. 1.

(22) Bazan, G.; Schrock, R. R.; Khosravi, E.; Feast, W. J.; Gibson, V. C. *Polymer Commun.* **1989**, *30*, 258.

(23) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.

(24) Risse, W.; Wheeler, D. R.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1989**, *22*, 3205.

(25) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423.

(26) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.

(27) Wagener, K. B.; Nel, J. G.; Konzelman, J.; Boncella, J. M. *Macromolecules* **1990**, *23*, 5155.

(28) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649.

(29) Wagener, K. B.; Brzezinska, K. *Macromolecules* **1991**, *24*, 5273.

(30) Wagener, K. B.; Smith, D. W. J. *Macromolecules* **1991**, *24*, 6073.

(31) Wagener, K. B.; Brzezinska, K.; Bauch, C. G. *Makromol. Chem. Rapid Comm.* **1992**, *13*, 75.

(32) Wagener, K. B.; Patton, J. T. *Macromolecules* **1993**, *26*, 249.

(33) Wagener, K. B.; Patton, J. T.; Forbes, M. D. E.; Myers, T. L.; Maynard, H. D. *Poly. Int.* **1993**, *32*, 411.

(34) Smith, D. W., Jr.; Wagener, K. B. *Macromolecules* **1993**, *26*, 1633.

(35) Smith, D. W.; Wagener, K. B. *Macromolecules* **1993**, *26*, 3533.

(36) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(37) Fox, H. H. Ph.D. Thesis, MIT, 1993.

(38) Fox, H. H.; Schrock, R. R. *Organometallics* **1994**, *13*, 635.

(39) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

(40) Feldman, J.; Murdzek, J. S.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2260.

(41) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384.

(42) Park, L. Y. Ph. D. Thesis, M.I.T., 1991.

(43) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organometal. Chem.* **1993**, *459*, 185.

(44) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004.

(45) Schrock, R. R. in "Reactions of Coordinated Ligands"; P. R. Braterman, Ed.; Plenum: New York, 1986.

(46) Schrock, R. R.; Feldman, J.; Cannizzo, L.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.

(47) Bradley, D. D. C. *J. Phys. D: Appl. Phys* **1987**, *20*, 1389.

(48) Braun, D.; Heeger, A. J. *J. Appl. Phys. Lett.* **1991**, *58*, 1982.

(49) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.

(50) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.

(51) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(52) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(53) Feast, W. J.; Gibson, V. C.; Khosravi, E.; Marshall, E. L.; Mitchell, J. P. *Polymer* **1992**, *33*, 872.

(54) Wittig, G.; Suchanek, P. *Chem. Ber.* **1967**, *100*, 347.

(55) Spangler, C. W.; Little, D. A. *J. Chem. Soc., Perkin Trans.1* **1982**, 2379.

CHAPTER 2

A New Type of Blue-Light Emitting Electroluminescent Polymer Prepared by ROMP

INTRODUCTION

Poly(*p*-phenylenevinylene) (PPV) has attracted much attention as an electroluminescent material.[1-11] PPV has several advantages as an emitting material in electroluminescence (EL) devices: a high quality thin film can be prepared by spin-coating a soluble precursor polymer, and the emission wavelength can be tuned by either changing the substituents on the arene ring[12] or by partially converting the precursor polymer, i.e., by generating PPV that contains relatively short conjugated chains.[8,9,11] The object in either case usually has been to increase the band gap and thereby generate a blue shifted emission spectrum.[4] A blue EL device is particularly desirable for several reasons.[13-15] In general compounds that have shorter conjugation lengths have a higher PL (photoluminescence) quantum yield. For example, 1,6-diphenylhexatriene shows an 80% PL quantum yield in cyclohexane, but 1,8-diphenyloctatetraene shows only a 9% PL quantum yield in the same solvent.[16] 1,4-Bis(4-isopropylphenylethenyl)benzene, a short analog of PPV, has a 94% PL quantum yield in cyclohexane,[16] while the PPV PL quantum yield is reported to take values ranging from a few percent[17] to 25%.[18,19] Thus, polymers that have short conjugated segments in the polymer chain would be expected to have a higher PL quantum yield; they might have a higher EL quantum yield also. Recently such an effect was observed in an alternating diblock copolymer.[20] An emitter that has a fixed conjugation length is most desirable, since a random distribution of conjugation lengths leads to broad emission bands. Pure blue-light emission therefore is relatively difficult to achieve under such circumstances.

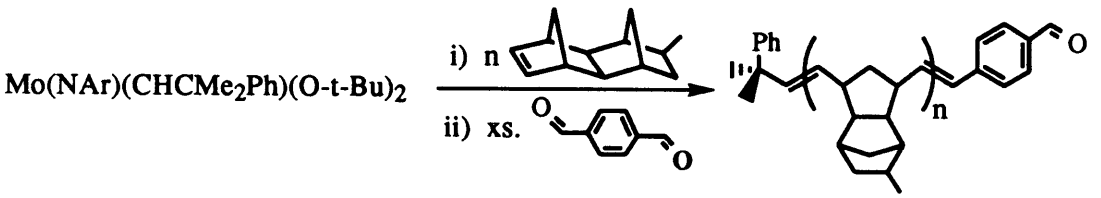
In the past several years well-defined molybdenum-based initiators for living ring opening metathesis polymerization (ROMP) have been developed.[21] Mo(N-2,6-i-Pr_2-C_6H_3)(CHCMe_2Ph)(O-t-Bu)$_2$ is an especially mild ROMP initiator that reacts readily with norbornenes or norbornadienes to give polymers in a controlled (living) manner with a resonable tolerance to the various functionalities.[21-23] In this chapter, the synthesis of polymers made by ROMP (employing Mo(N-2,6-i-Pr_2-C_6H_3)(CHCMe_2Ph)(O-t-Bu)$_2$ as

the initiator) that contain a short conjugated emitter unit either in the main chain or as a side chain is discussed and their PL and EL properties are investigated.

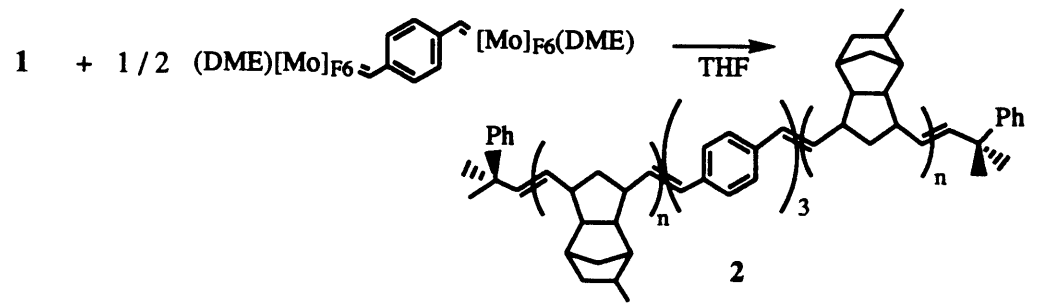
RESULTS AND DISCUSSION

Triblock copolymers containing emitter in the main chain

Short oligomers of PPV are highly insoluble.[24] Therefore the first approach to prepare "soluble" PPV oligomers is analogous to the method that was used previously to prepare "soluble" unsubstituted polyenes;[25,26] polymethyltetracyclododecene (polyMTD) was employed as a solubilizing chain in a block copolymer. Living polyMTD was treated with excess terephthaldehyde to yield aldehyde-capped polyMTD (**1**) that contained up to 100 equivalents of monomer (eq 2.1). The aldehyde-capped



1; n = 10, 25, 50, 100



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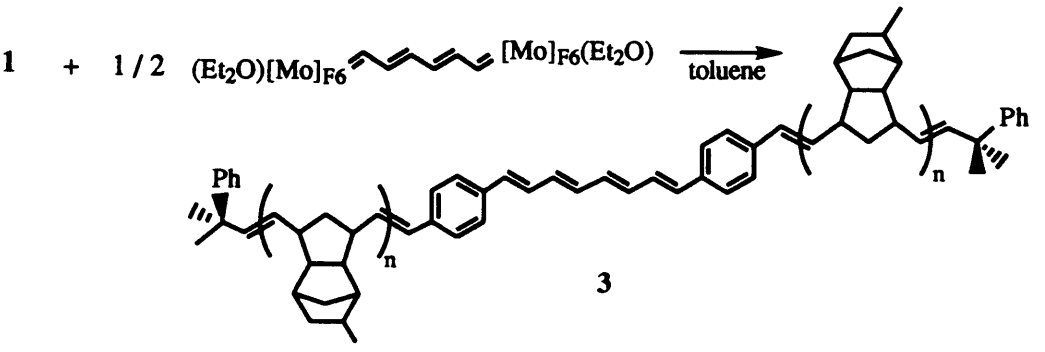
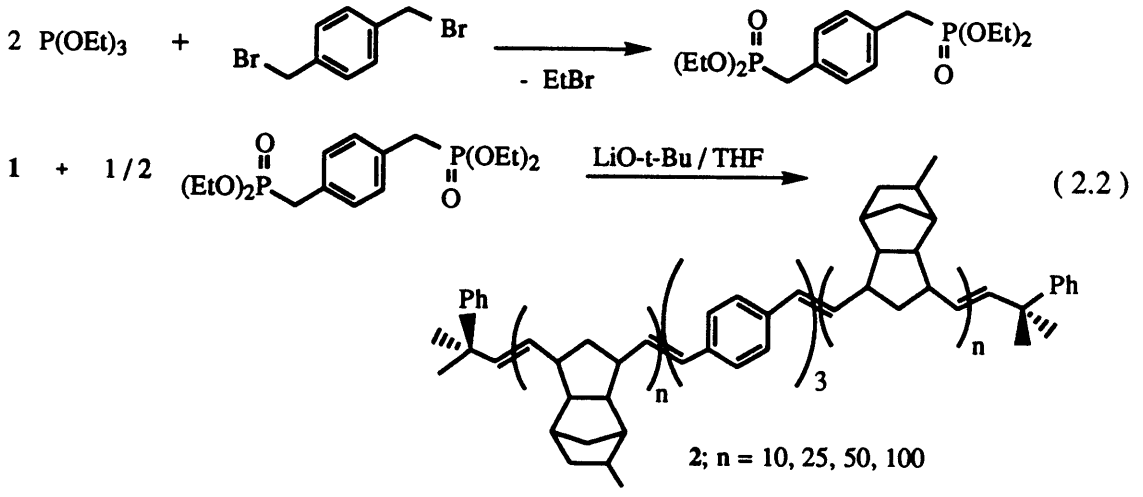
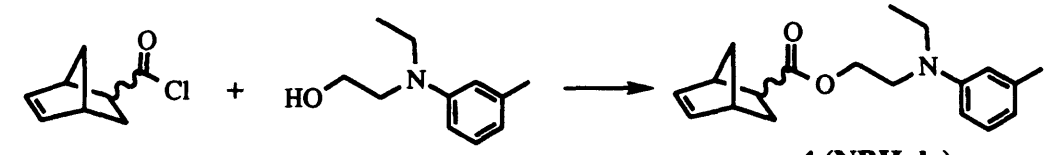


polyMTD was then treated with half equiv of conjugated difunctional alkylidene complexes which were described in Chapter 1. The reaction of half equiv of {(DME)-$[Mo]_{F6}$=CH}$_2C_6H_4$ [27,28]($[Mo]_{F6}$ = Mo(N-2,6-i-Pr_2-C_6H_3)($CHCMe_2Ph$)(OR_{F6})$_2$) and an aldehyde-capped polyMTD produced a coupled product (**2**), which showed a strong blue photoluminescence under the long wavelength (366 nm) UV irradiation. However the yield of coupled triblock copolymers was not high enough, probably due to impurities in the aldehyde-capped polyMTD. When 0.5 equiv of {(Et_2O)$[Mo]_{F6}$=CH}$_2(CH)_4$ was treated with an aldehyde-capped polyMTD, the coupled triblock polymer (**3**) could be isolated by the fractionation in a THF / methanol mixture. However this triblock copolymer did not show strong PL consistent with a previously reported result.[16] In order to solve the problem of the high sensitivity of conjugated difunctional alkylidene complexes toward impurities in the aldehyde-capped polyMTD, a bis-Wittig reagent[29-31] was prepared from triphenylphosphine and α,α'-dibromo-*p*-xylene. Unfortunately this reagent is insoluble in common polymerization solvents such as toluene and THF. A bisphosphonate analog[32-35] prepared from triethyl phosphite and α,α'-dibromo-*p*-xylene showed high solubility in THF. The aldehyde-capped polyMTD was then treated with 0.5 equiv of the bisphosphonate compound to generate triblock copolymers (**2**) that have a phenylene vinylene "trimer" in the middle of the polymer chain (eq 2.2). These soluble

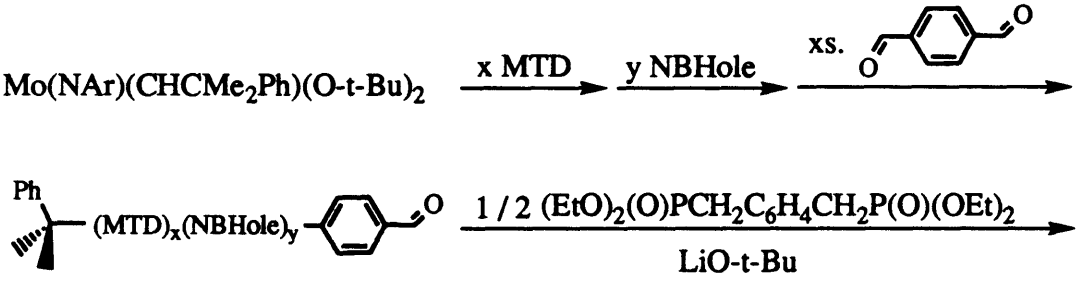


(2.2)

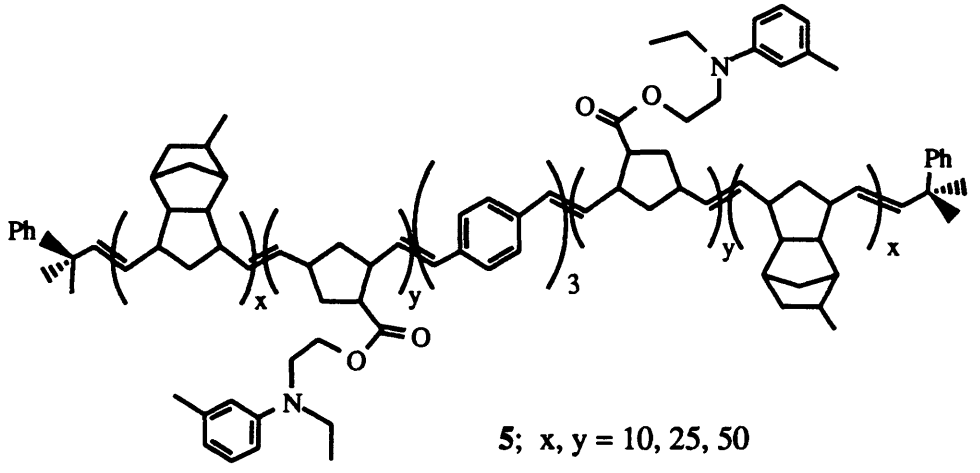
polymers showed a λ_{max} in the absorption spectrum in THF at 384 nm and in the emission spectrum at 455 nm. A preliminary measurement of the PL quantum yield compared to an anthracene standard was relatively high (66%), but no EL was detected from a single layer ITO / polymer / Al device prepared by professor Richard H. Friend's group. It can be explained that this is simply a consequence of the low concentration of the emitter. (The maximum concentration of the emitter is only 8% by weight.) In order to increase the mobility of charge carrier through the whole polymer, a new monomer (**4**, NBHole) that contains a hole transport material, N,N-diethyl-2-methylaniline,[36] was prepared, copolymerized with MTD, and the resulting copolymer was capped with excess terephthaldehyde (eq 2.3). Pentablock copolymer (**5**) prepared from this aldehyde-capped



4 (NBHole)



(2.3)



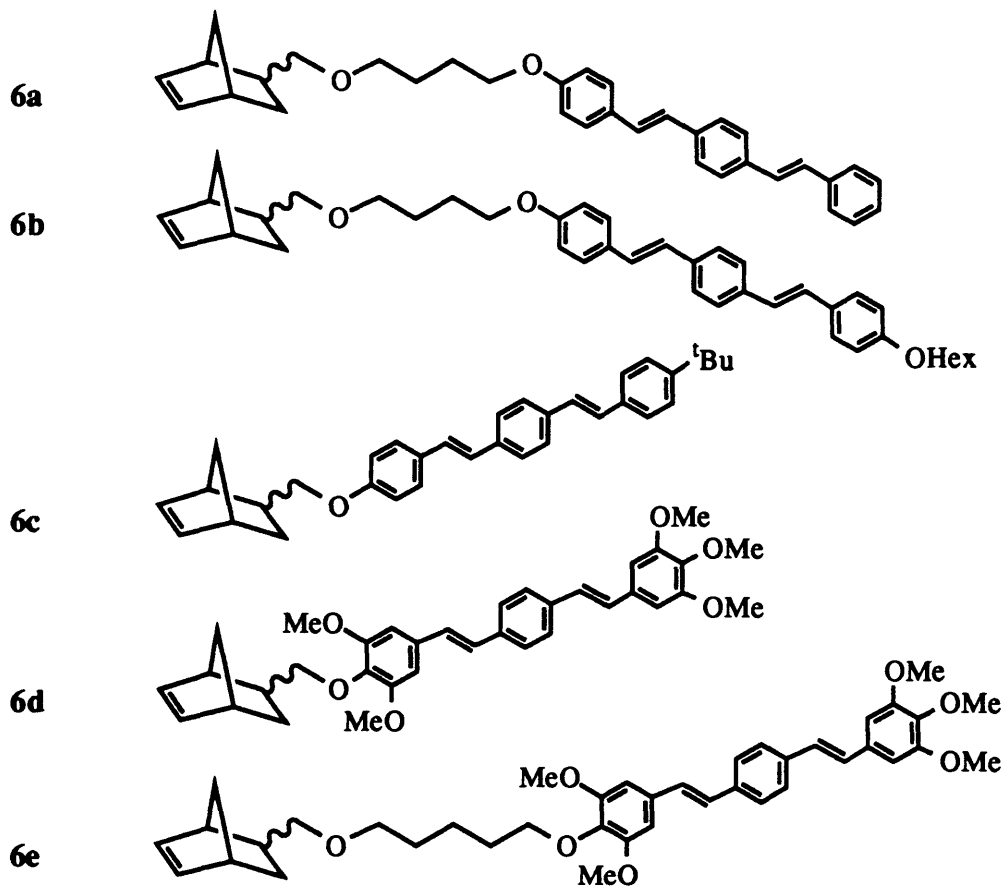
5; x, y = 10, 25, 50

polymer, however, did not show EL either. In short, the majority of the polymer is an insulator in which holes and electrons cannot migrate, find one another, and generate an emissive excited state.

New EL polymers containing an emitter as a side chain

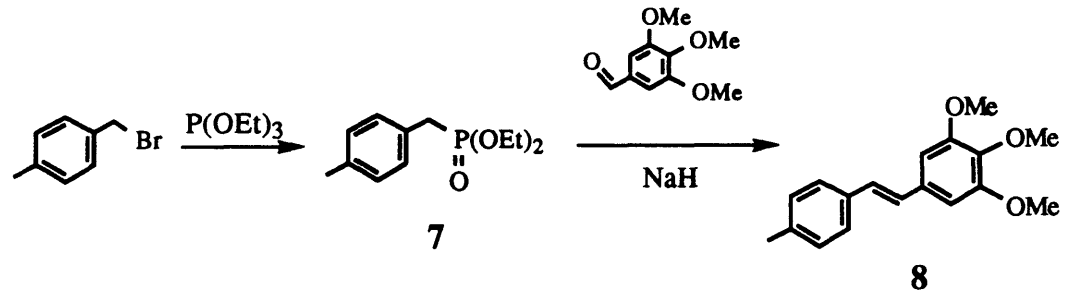
In order to increase the number of emitters in the polymer, monomers that contain one chromophore per monomer were prepared (Scheme 2.1). Monomer **6a** was prepared from 5-norbornene-2-methanol and benzyl bromide in several steps (similar to the synthesis of **6e** shown in eq 2.4), but it was only slightly soluble in THF. Modified

Scheme 2.1. Monomers which contain chromophore.



NBTPV-C5

monomers (**6b** and **6c**) which have alkyl substituents on the one of the phenyl ring did not improve solubility. Attempted polymerization of **6a**, **6b**, and **6c** in THF employing $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ (Ar = 2,6-i-Pr_2-C_6H_3) was relatively unsuccessful, as the polymer precipitated out during the reaction. Consequently yields were low and the resulting polymer had a broad molecular weight distribution. Evidently the inherently high solubility of a polymer prepared from a 5-substituted norbornene is not great enough to outweigh the contribution of a relatively insoluble side chain. Another monomer (**6d**) which has five more methoxy groups on the phenyl rings was very soluble in THF (1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene has been reported to be relatively soluble in common solvents[37]), but polymerization of this monomer failed, probably as a consequence of the steric bulkiness around the living alkylidene. The most successful monomer of these was NBTPV-C5 (**6e**). The synthesis of **6e** proceeded with an overall yield of 17% (eq 2.4). NBTPV-C5 (**6e**) could be polymerized smoothly to give (after capping with benzaldehyde) a soluble low polydispersity polymer in high yield (Scheme 2.2). This polymer has a λ_{max} = 368 nm in the absorption spectrum in THF solution. Films of poly(**6e**) could be prepared by static casting form THF or chloroform. For the cast film λ_{max} = 362 nm for absorption and 475 nm for emission. Once a good film making polymer was obtained, EL measurements were carried out with collaboration of Professor Friend's group in England. Polymer films of 150 - 200 nm thickness was prepared by spin coating on a glass substrate covered with an ITO conducting layer (anode) onto which the calcium electrode (cathode) was then evaporated in vacuo. Since the EL and PL spectra for films prepared in this manner were similar (Figure 2.1), the origin of the emitting light in each spectrum is likely to be the same. This single layer device showed a turn-on voltage at ~12 V (Figure 2.2a) and an EL efficiency of 0.3%. The linear relationship between luminance and current (Figure 2.2b) is strong evidence that the light is generated by recombination of electrochemically generated holes and electrons.



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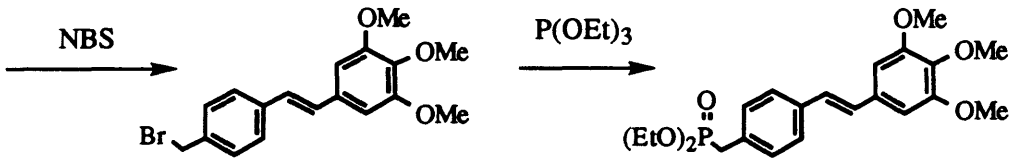
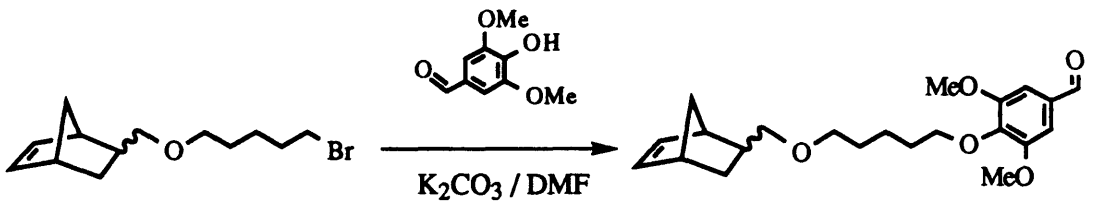


9 10 (2.4)



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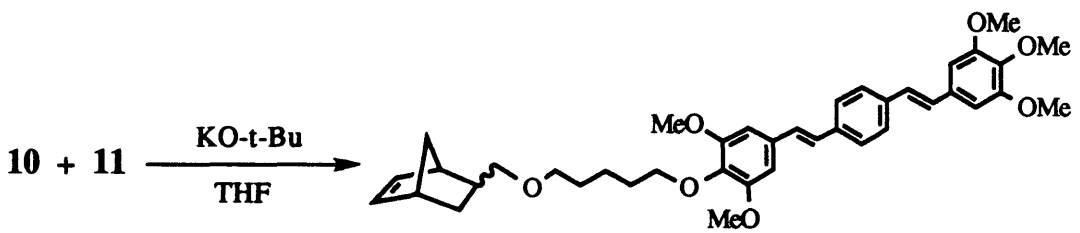
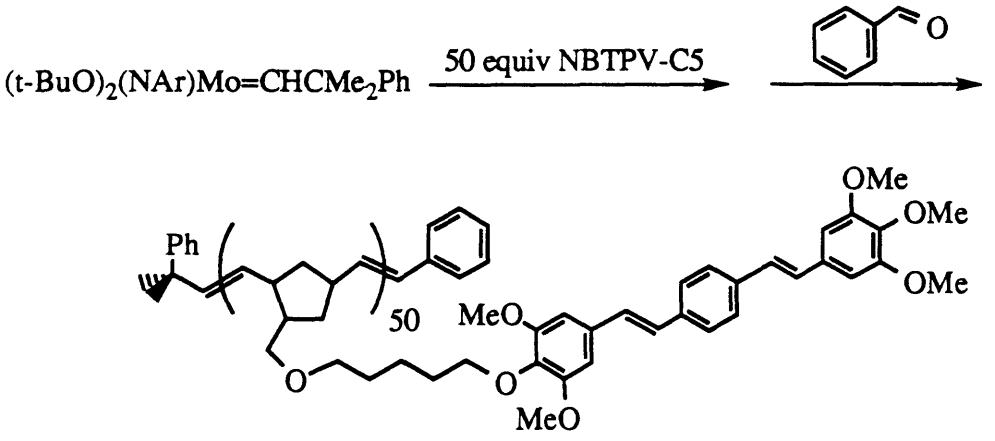


NBTPV-C5 (6e)

Scheme 2.2. Preparation of polyNBTPV-C5 50 mer.



PolyNBTPV-C5 50mer (M_w / M_n = 1.10)

$\lambda_{max,abs}$ = 368 nm (in THF)
362 nm (cast film)

$\lambda_{max,em}$ = 475 nm (cast film)

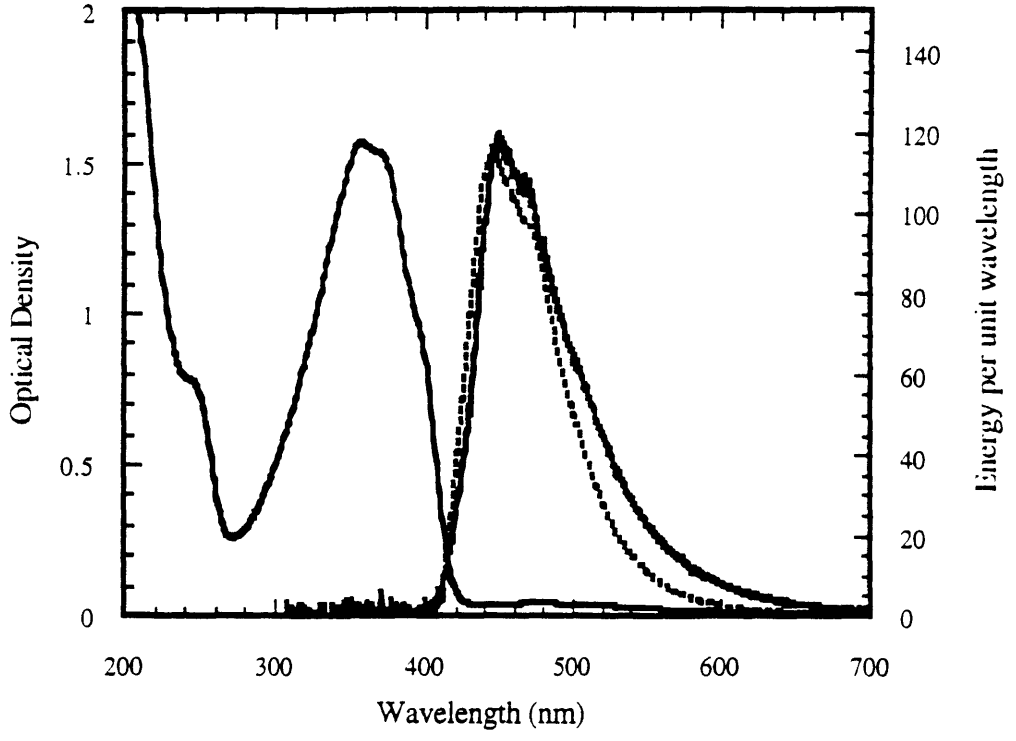


Figure 2.1. PL(broken line), EL and absorption of NBTPV-C5 50mer.

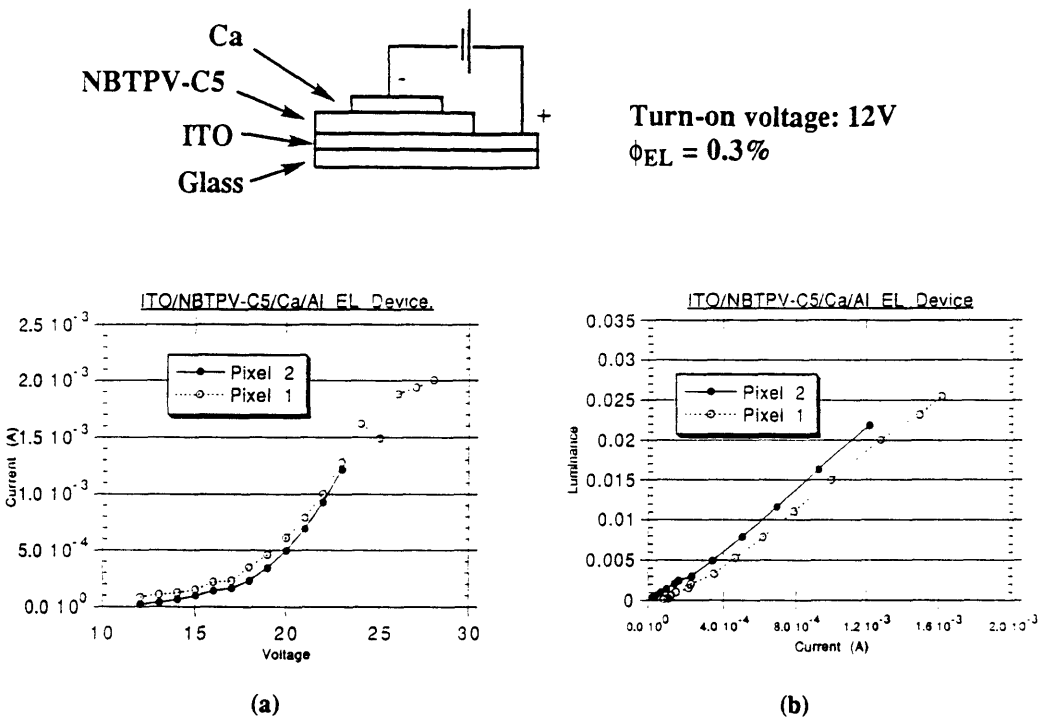


Figure 2.2. Single layer EL device (ITO / PolyNBTPV-C5 / Ca).
a) Relationship between current and luminance.
b) Relationship between current and voltage.

Another single layer device was prepared in which biphenyl-*t*-butylphenyl-oxadiazole (t-PBD), an electron transport material,[38,39] was dissolved in solution along with the polymer before spin coating. It showed a higher EL efficiency (0.55%) with a turn-on voltage at 17 V. When a classically prepared film of PPV [1] was introduced as a hole transport material between the ITO and emitter layers, the turn-on voltage was about the same (15V) but the EL efficiency was reduced to 0.21%. The low EL efficiency might be ascribed to reabsorption of emitted light by the PPV layer. The fact that the emitted light is green-blue instead of blue supports this proposal.

In all experiments a significant problem was the relatively short lifetime (several minutes). A cyclic voltammogram of **6e** in acetonitrile showed an irreversible oxidation peak at 0.92 V vs. SCE and a quasi-reversible reduction peak at -2.17 V, while poly(**6e**)

in THF showed similar peaks at 0.82 V and -2.18 V (Figure 2.3). After several scans from 1.5 V to -2.4 V the first oxidation peak disappeared in each case. An electrochemiluminescence (ECL) experiment of **6e** in acetonitrile with an ITO electrode showed a flash of blue light emitting from the solution near the electrode surface when the voltage was swept from 1.8 V to -2.5 V with a speed of 5 cycles / sec, but the ECL dimmed and stopped after ~10 sec. At this point a yellowish material covered the surface of the ITO electrode. ECL could be observed again after the yellowish material had been gently removed from the electrode surface with a tissue, but again ECL decayed rapidly. The short lifetime of the EL device containing polyNBTPV-C5 most likely results from the electrochemical instability of the emitter.

Electrochemically more stable emitter systems .

In order to test the proposal that the short lifetime of EL device of polyNBTPV-C5 results from the electrochemical instability of the emitter, new more electrochemically stable blue-light emitters were sought. There are two other fields which are closely related with electroluminescence. Dye-lasers[40] produce light by stimulated emission from the excited singlet state (S_1) to the ground state (S_0). The fluorescent quantum yield highly depends on the structure and the photochemical stability of the dye molecules, and several rigid organic dyes are known to have very high fluorescent quantum yield. Coumarin derivatives (**12**) are one of the widely used dyes for blue-light emitting dye-laser.[41,42] The other field is electrochemiluminescence (ECL) which is even more closely related with electroluminescence (EL).[43] Recombination of the electrochemically reduced species (radical anion) with electrochemically oxidized species (radical cation) in a solution produces the excited singlet state (S_1) and the radiative decay to ground state (S_0) generates the light. The stabilities of radical anion and radical cation are very important in ECL. 9,10-Diphenylanthracene (**13**) has been studied for ECL and its electrochemical properties are well understood.[44-46]

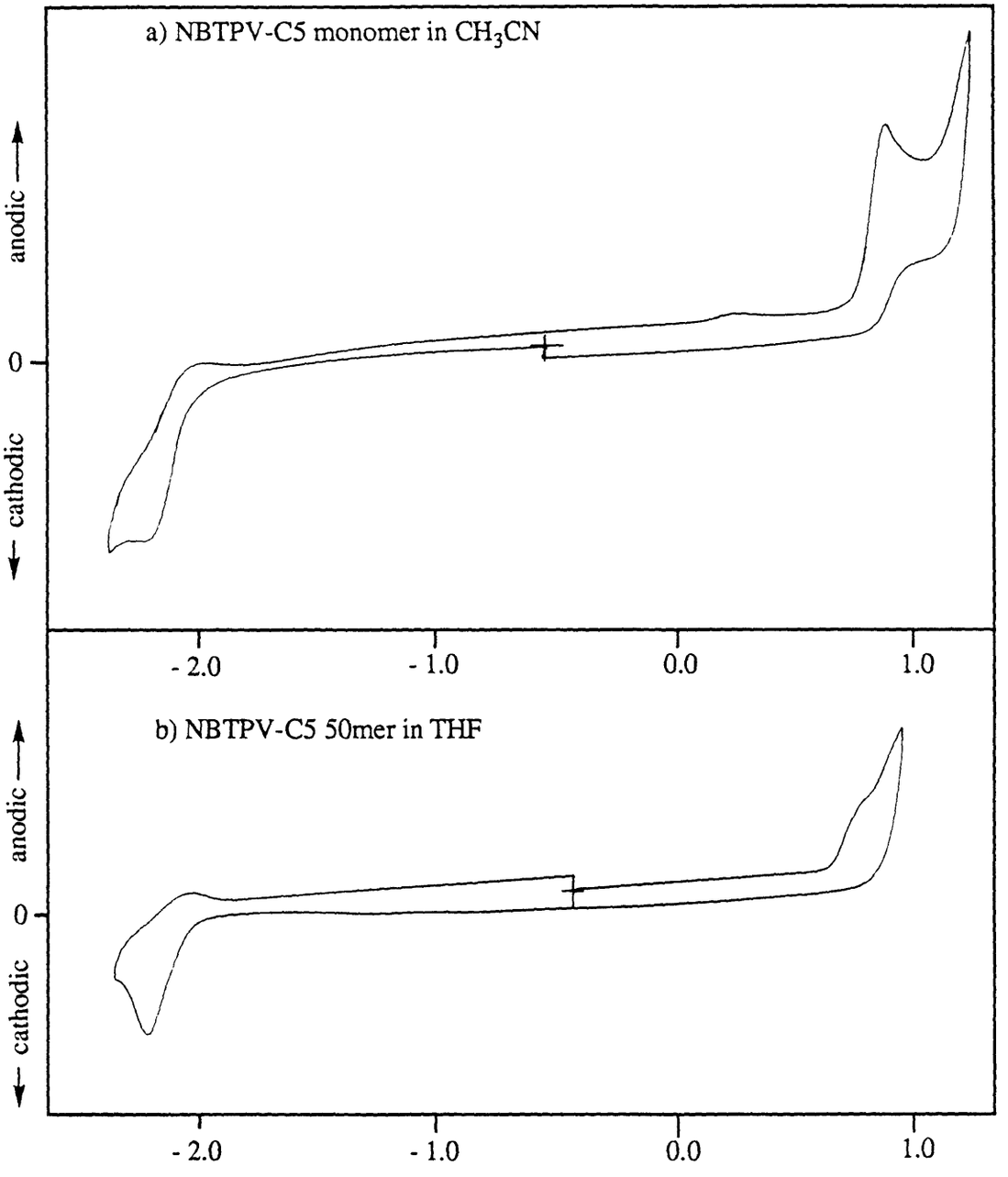
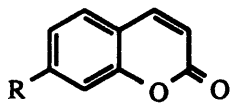
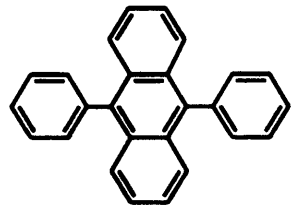


Figure 2.3. Cyclic voltammetry of (a) NBTPV-C5 monomer in CH_3CN / 0.1 N $[n\text{-}Bu_4N]^+PF_6^-$ and (b) NBTPV-C5 50mer in THF / 0.1 N $[n\text{-}Bu_4N]^+$ PF_6^- at 200 mVs^{-1} at a 500 μm Pt disk electrode.



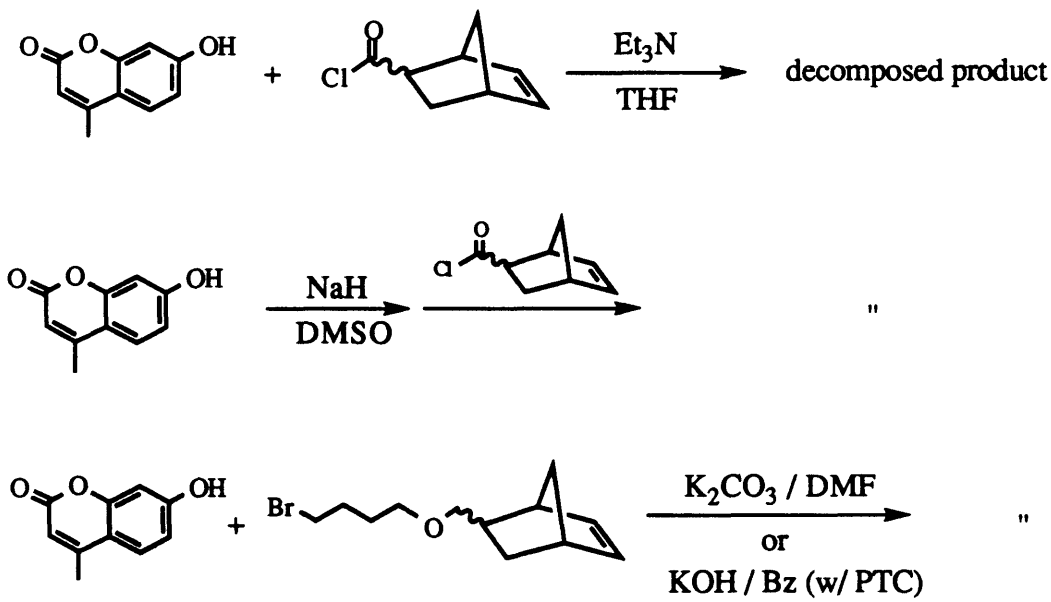
R = NR'_2 or OR'

12



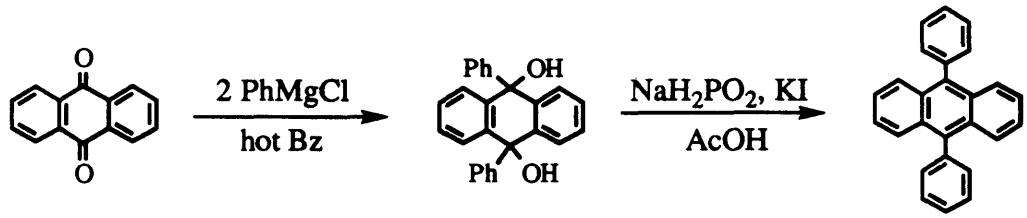
13

New monomers which contain an electrochemially more stable emitter such as coumarin or 9,10-diphenylanthracene are expected to be stable in the high electric field of an EL device and should have high EL quantum yields with long lifetimes. Several attempts to introduce coumarin as an emitter into the norbornene monomer system were unsuccessful probably due to the decomposition of the ester linkage of coumarin under basic reaction conditions (eq 2.5). 9,10-Diphenylanthracene (**13**, DPA) was prepared

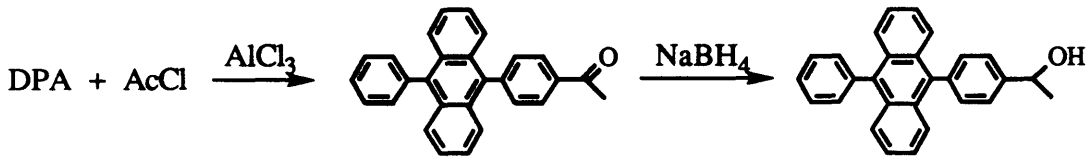


(2.5)

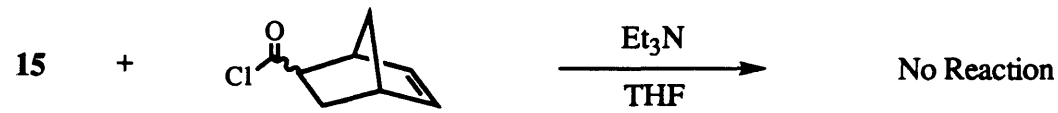
from anthraquinone and derivatized to introduce the functional group which could couple with available norbornene monomer precursors (eq 2.6). 9-(4-Hydroxyethyl)phenyl-10-phenylanthracene (**15**) was synthesized in good yield, but did not react with 5-



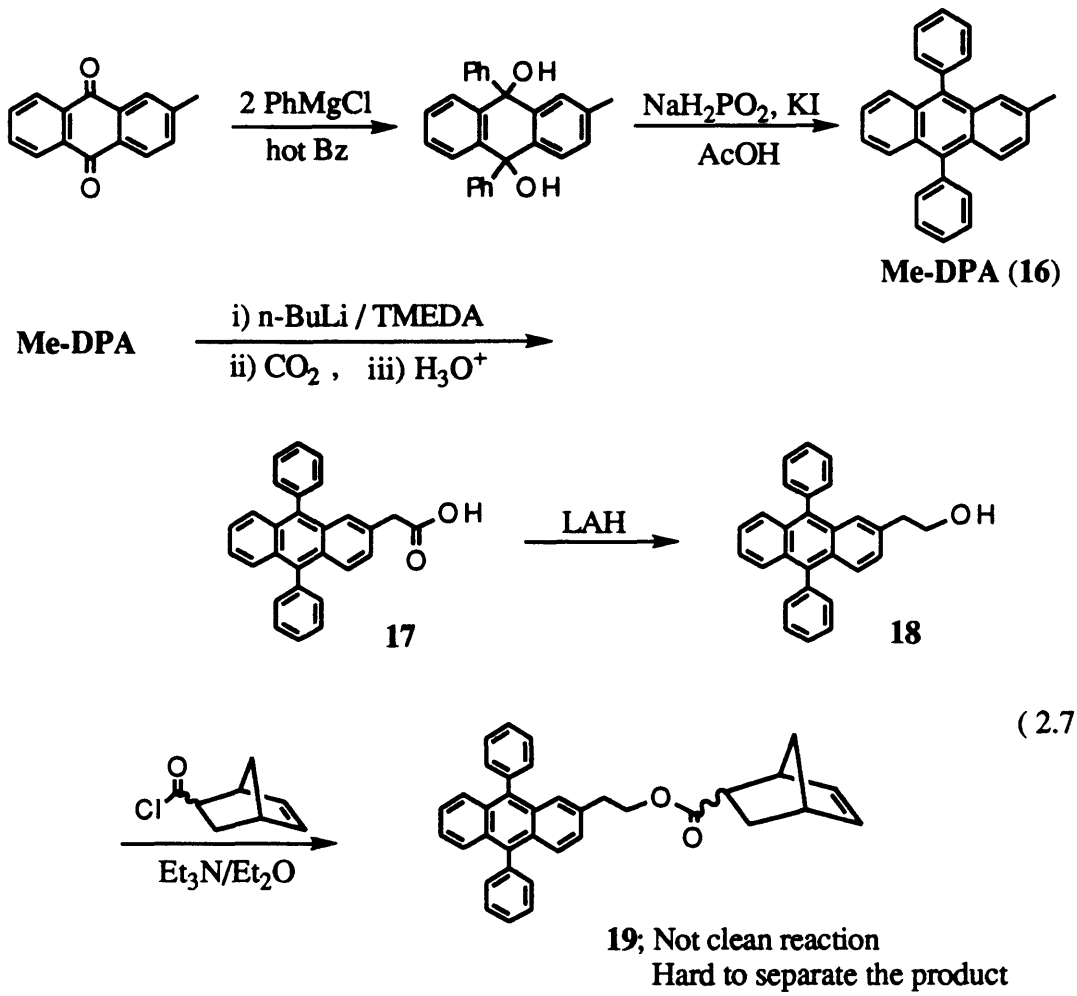
DPA (13)



14 **15** (2.6)

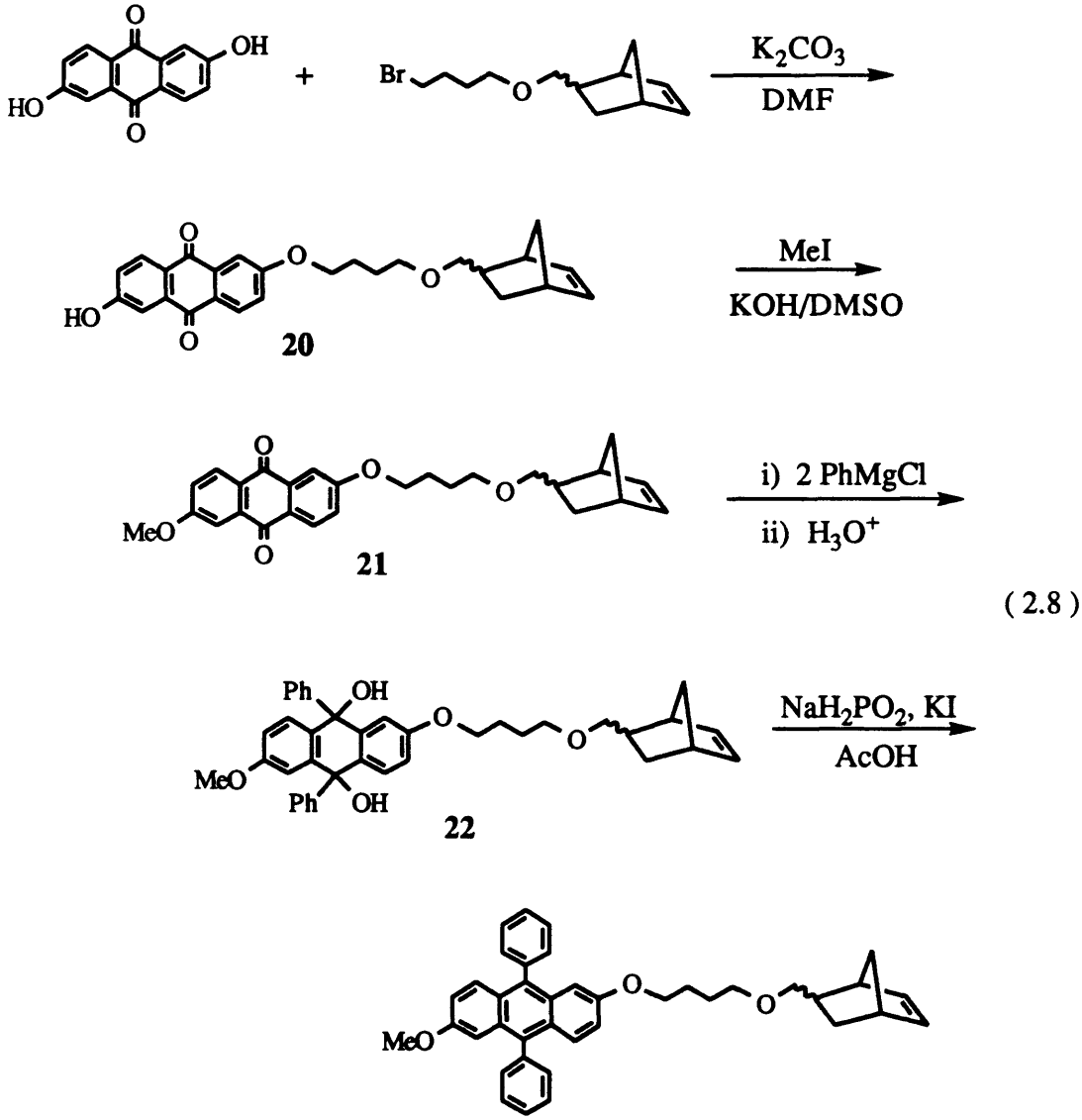


norbornenecarbonyl chloride or 5-(4-bromobutoxy)methylnorbornene due to the steric crowdedness of the secondary alcohol. In order to make primary alcohol derivative of DPA, 2-methyl-9,10-diphenylanthracene (**16**) was prepared in a same way and carboxylated after metallation at the benzylic position (eq 2.7). The resulting DPA-CH_2CH_2OH (**18**) was treated with 5-norbornenecarbonyl chloride to give the expected coupled product. However purification of the monomer to polymerization grade was unsuccessful. An alternate route was attempted to introduce the DPA unit into the norbornene system, anthraquinone was attached to norbornene first and then two phenyl groups were introduced by reacting phenyl Grignard reagent followed by reduction (eq



(2.7)

2.8). 2,6-Dihydroxyanthraquinone was treated with 5-(4-bromobutoxy)methyl-norbornene to give coupled product (**20**). Another hydroxy group was protected as a methoxy group, and the two phenyl groups were introduced using phenyl Grignard reagent. Reduction of the resulting diol compound (**22**) with KI and NaH_2PO_2 in acetic acid generated the DPA unit and the reaction mixture showed strong blue photoluminescence. Unfortunately, purification of this new monomer (**23**) is difficult due to lack of crystallinity. Furthermore, the impurity is very similar to the product and the two cannot be separated by TLC or recrystallization. Polymer prepared from this impure monomer had very broad molecular weight distribution.



(2.8)

23; Hard to purify
UV showed two different absorptions

In addition to the low yield of the reaction with the phenyl Grignard reagent which might generate the main impurities, the problem of the synthesis of new efficient electroluminescent monomer seems to be the purification to get polymerization grade monomer. In order to overcome these problems, a new monomer system that has more crystalline and/or rigid structure must be designed.

CONCLUSIONS

Several polymers that have a short conjugated emitter unit in the main chain or as a side chain can be prepared by ring opening metathesis polymerization (ROMP) employing $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ as the initiator. The polymers that have only one emitter unit in the middle of the polymer chain can show a strong photoluminescence with a high PL quantum yield but no electroluminescence. This result illustrated the importance of the charge mobility (conductivity) in EL devices. Other types of EL polymers prepared from the monomer (NBTPV-C5) that has an emitter unit per monomer in a living manner, show a strong PL and EL. The EL device from this polymer shows up to 0.55% EL efficiency, which is the best reported result so far for a blue-light emitting EL device.

A significant problem of this device is the relatively short lifetime, perhaps due to the electrochemical instability of the emitter. New monomers which contain a more electrochemically stable emitter (9,10-diphenylanthracene) were prepared, but attempts to make a narrow polydispersity polymer failed as a consequence of the monomer being impure.

In theory a variety of emitter groups could be introduced as a side chain in the norbornene monomer system and a wide variety of EL materials could be prepared by the ROMP method. Since ROMP that employs $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ as the initiator is living, block copolymers can be prepared from monomers that contain emitter and hole- or electron-transporting group as side chains. Therefore films that contain emitters and hole- or electron-transporting side chains in specific morphologies (layers, rods, spheres) could be prepared and the electroluminescent properties of these films examined.

EXPERIMENTAL PROCEDURES

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric acid / nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade THF was vacuum transferred a second time from sodium benzophenone ketyl. Polymerization grade toluene was stored over sodium / potassium alloy and passed through alumina prior to use.

HPLC grade solvents were used in Gel permeation chromatography (GPC) runs and were degassed prior to use. GPC was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Viscotek Differential Refractometer / Viscometer H-500, and a Spectroflow 757 absorbance detector on a samples 0.1 - 0.3% (w/v) in THF which were filtered through a Millex-SR 0.5μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 - 2.75 x 10^6. Elemental analysis (C, H) was performed on a Perkin-Elmer 2400 CHN analyzer. NMR data were obtained at 300 MHz and listed in parts per million downfield from tetramethylsilane. Spectra were obtained at 25°C unless otherwise noted.

All chemicals used were reagent grade and were purified by standard methods. $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$,[22] 5-norbornenecarbonyl chloride[47], $[(DME)(R_{F6}O)_2(ArO)Mo{=}CH]_2C_6H_4$ and $[(Et_2O)(R_{F6}O)_2(ArN)Mo{=}CH]_2(CH)_4$ [27,28] were prepared as described in the literature. Benzaldehyde was distilled over Na and stored at -35°C. Silica gel (70 - 230 mesh, 60Å) was used as received from Aldrich.

PL and EL measurements were carried out in the collaboration with Derek R. Baigent of professor Richard H. Friend's group in England. EL devices were prepared by the same method reported in the literature.[1] Measurements of current and luminance as a

function of applied field were made under forward bias. A calibrated silicon photodiode was used to measure light output in the forward direction from the device. Electroluminescence and photoluminescence spectra were taken using a spectrograph coupled to a Peltier-cooled CCD array (ORIEL Instaspec IV). The system response was calibrated using a tungsten lamp. Excitation for the photoluminescence was from the multi-line UV mode of an argon ion laser. The internal quantum efficiency of these devices was calibrated from measurements of the current and of the light output in the forward direction. Light emission within the polymer film was assumed to be isotropic, and refraction at the polymer interface was taken into account when calculating the internal quantum efficiency[48]. The refractive index of a NBTPV-C5 50mer film was measured using prism coupling of light into the optical waveguide modes, and was found to be approximately 1.7.

$PhMe_2CCH(MTD)_nCHC_6H_4CHO$ (1). The preparation of the polymer in which n = 50 (on average) is provided as an example. $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ (20.0 mg, 42.9 μmol) was dissolved in 3 mL of toluene. MTD (373 mg, 2.14 mmol) was dissolved in 1 mL of toluene and added all at once to a stirred solution containing the catalyst. After 15 min, terephthaldehyde (58.0 mg, 429 μmol) was added and the solution was stirred for 1h. The polymer was isolated by the precipitation into methanol; yield 351 mg (92%). Other polymers (n = 10, 25, 100) were prepared similarly.

$(EtO)_2(O)PCH_2C_6H_4CH_2P(O)(OEt)_2$. $P(OEt)_3$ (6.71 g, 40.0 mmol) was mixed with α,α'-dibromo-*p*-xylene (5.44 g, 20.0 mmol) and the mixture was heated to 100°C for 5h. Above 80°C, EtBr was generated and collected in a Dean-Stark trap. The reaction mixture was cooled to room temperature and 8.2 g of crude solid product was obtained. Recrystallization from THF gave 6.13 g (81%) of the bisphosphonate compound: ^1H NMR (C_6D_6) δ 7.33 (s, 4, H_{aryl}), 3.80 (m, 8, -OCH_2), 2.93 (d, 4, -CH_2P(O)-), 0.93 (t, 12, -CH_3).

Triblock copolymers from $[(DME)(R_{F6}O)_2(ArO)Mo{=}CH]_2C_6H_4$ (2). These polymers were prepared by two routes as described below. a) A solution containing an aldehyde-capped polyMTD$_{100}$ (357 mg, 20.1 μmol) in 15 mL of THF was mixed with a solution of a difuntional alkylidene complex, $[(DME)(ArN)(R_{F6}O)_2Mo{=}CH]_2C_6H_4$ (17.0 mg, 10.0 μmol), in 5 mL of THF and the mixture was stirred for 1h. The polymer was precipitated from methanol and dried in vacuo. GPC of the resulting polymer showed about 21% conversion. b) The preparation of the polymer in which n = 10 (on average) is provided as an example. A solution containing the aldehyde-capped polyMTD$_{10}$ (350 mg, 183 μmol), bisphosphonate (29.0 mg, 92.0 μmol) and LiO-t-Bu (29.0 mg, 366 μmol) in 30 mL of THF was refluxed for 24h. The product was precipitated into MeOH and fractionated in THF/MeOH mixture; yield 140 mg (40%) of pale-yellow polymer. the GPC of this polymer (in THF versus polystyrene standards) showed a unimodal peak with a polydispersity of 1.12.

Triblock copolymers from $[(Et_2O)(R_{F6}O)_2(ArN)Mo{=}CH]_2(CH)_4$ (3). A solution of an aldehyde-capped polyMTD$_{100}$ (352 mg, 20.0 μmol) in 4 mL of toluene was mixed with a solution of a conjugated difunctional alkylidene complex, $[(Et_2O)(ArN)(R_{F6}O)_2Mo{=}CH](CH)_4$ (15.0 mg, 10.0 μmol) in 1 mL of toluene and the mixture was stirred for 1h. The product was precipitated into methanol and dried in vacuo. GPC of the product showed 79% conversion and the coupled product (123 mg, 35%) was fractionated in THF/methanol mixture.

NBHole (4). A solution of 5-norbornenecarbonyl chloride (1.88 g, 12.0 mmol) in 10 mL of THF was added to a mixture of 2-(N-ethyl-*m*-toluidino)ethanol (1.97 g, 11.0 mmol) and triethylamine (1.21 g, 12.0 mmol) in 40 mL of THF. The mixture was refluxed for 20h and solvent was removed in vacuo. The residue was dissolved in $CHCl_3$ and worked up with water. The organic layer was separated and dried over $MgSO_4$. Solvent was removed in vacuo to give greenish-yellow liquid which was purified by column chromatography (alumina, toluene/hexane = 3/2) to give colorless liquid product

(2.68 g, 81%, endo/exo = 3/1): ^{1}H NMR (C_6D_6, endo isomer) δ 7.19-7.10 and 6.62-6.49 (m, 4, H_{aryl}), 6.06-5.95 (m, 2, H_{vinyl}), 4.15-4.00 (m, 2, -OC*H*$_2$-), 3.28-3.20 (t, 2, -C*H*$_2$N-), 3.06 (q, 2, -NC*H*$_2$-), 2.23 (s, 3, C*H*$_3$), 0.90 (t, 3, C*H*$_3$), plus resonances in the 3.02-0.90 ppm region that are similar to those in the starting materials; ^{1}H NMR (C_6D_6, exo isomer) δ 7.19-7.10 and 6.61-6.48 (m, 4, H_{aryl}), 5.93-5.85 (m, 2, H_{vinyl}), 4.12 (t, 2, -OC*H*$_2$-), 3.26 (t, 2, -C*H*$_2$N-), 3.05 (q, 2, -NC*H*$_2$-), 2.23 (s, 3, C*H*$_3$), 0.90 (t, 3, C*H*$_3$), plus resonances analogous to the starting materials in the 3.01-1.15 ppm region.

[PhMe$_2$CCH(MTD)$_x$(NBHole)$_y$CH]$_2$(CHC$_6$H$_4$CH)$_3$ (5). The preparation of the polymer in which x, y = 10 (on average) is shown below as an example. Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ (46 mg, 84 μmol) was dissolved in 2 mL of toluene. A solution of MTD (146 mg, 0.84 mmol) in 1 mL of toluene was added all at once to a stirred solution of catalyst. After the mixture was stirred for 30 min, a solution of NBHole (256 mg, 0.84 mmol) in 1 mL of toluene was added and the mixture was stirred for another 30 min. Terephthaldehyde (115 mg, 850 μmol) was added and the mixture was stirred for 1h. The polymer was precipitated from methanol and dried in vacuo; yield 405 mg (92%), PDI = 1.11 in THF versus polystyrene standards. Other polymers (x,y = 25, 50) were prepared similarly.

A solution of aldehyde-capped polymer (406 mg, 81.0 μmol), bisphosphonate (13.0 mg, 42.0 μmol) and LiO-t-Bu (13.0 mg, 162 μmol) were mixed in 20 mL of THF and the mixture was refluxed for 24h. The product was precipitated into methanol and fractionated in a $CHCl_3$/MeOH mixture; yield 267 mg (66%), PDI = 1.16 in THF versus polystyrene standards.

Synthesis 6a; (EtO)$_2$P(O)CH$_2$C$_6$H$_5$. Benzyl bromide (10.26 g, 60.0 mmol) and triethyl phosphite (10.97 g, 66.0 mmol) were mixed and the mixture was heated at 100°C for 5h; ethyl bromide was removed in a Dean-Stark trap. Excess triethyl phosphite was removed in vacuo to give product (EtO)$_2$P(O)CH$_2$C$_6$H$_5$ (13.8 g, 100%): ^{1}H NMR ($CDCl_3$) δ 7.30-7.15 (m, 5, H_{aryl}), 3.95 (m, 4, OC*H*$_2$-), 3.08 (d, 2, C*H*$_2$P), 1.18 (t, 6,

CH_3).

$CH_3C_6H_4CH=CHC_6H_5$. $(EtO)_2P(O)CH_2C_6H_5$ (13.8 g, 60.0 mmol) and *p*-tolualdehyde (7.21 g, 60.0 mmol) were added to a suspension of NaH (80% dispersion in mineral oil, 2.16 g, 90.0 mmol) in a mixture of 100 mL of THF and 20 mL of DMF and the mixture was refluxed for 5h. The reaction was worked up with water and the organic layer was extracted into Et_2O. The ether extract was dried over $MgSO_4$. Precipitation into water gave pure $CH_3C_6H_4CH=CHC_6H_5$ (11.44 g, 98%): ^1H NMR ($CDCl_3$) δ 7.4-7.0 (m, 9, H_{aryl}), 6.93 (s, 2, H_{vinyl}), 2.20 (s, 3, CH_3).

$BrCH_2C_6H_4CH=CHC_6H_5$. A mixture of $CH_3C_6H_4CH=CHC_6H_5$ (11.44 g, 58.9 mmol) and NBS (11.53 g, 64.8 mmol) in 60 mL of CCl_4 with a catalytic amount of AIBN was refluxed for 5h . The mixture was cooled to room temperature and worked up with water. The product was extracted into $CHCl_3$ and the extract was dried over $MgSO_4$. The solvent was removed in vacuo to give the crude solid product, which was dissolved in THF and isolated by precipitation into hexane; yield 38.53 g (53%): ^1H NMR ($CDCl_3$) δ 7.50-7.19 (m, 9, H_{aryl}), 7.06 (m, 2, H_{vinyl}), 4.48 (s, 2, CH_2Br).

$(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_5$. $BrCH_2C_6H_4CH=CHC_6H_5$ (8.53 g, 31.3 mmol) and triethyl phosphite (5.99 g, 36.0 mmol) were dissolved in 100 mL of toluene and the mixed solution was heated at 100°C for 17h. Solvent and excess triethyl phosphite were removed in vacuo to give 9.9 g (96%) of $(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_5$: ^1H NMR ($CDCl_3$) δ 7.51-7.18 (m, 9, H_{aryl}), 7.03 (s, 2, H_{vinyl}), 3.98 (m, 4, OCH_2-), 3.12 (d, 2, CH_2P), 1.21 (t, 6, CH_3).

4-[4-(5-Norbornenylmethoxy)butoxy]benzaldehyde. 4-(5-Norbornenylmethoxy)butyl bromide (7.10 g, 27.4 mmol) and 4-hydroxybenzaldehyde (3.51 g , 28.8 mmol) were added to a suspension of NaH (0.99 g, 32.9 mmol) in 100 mL of DMF and the reaction mixture was stirred for 3.5h. The mixture was worked up with a saturated NH_4Cl solution at 0°C and the product was extracted into Et_2O. Pure product (3.97 g, 48%) was isolated by column chromatography (silica gel, Et_2O/pentane = 1/10): ^1H NMR ($CDCl_3$)

δ 99.83 (s, 1, C*H*O), 7.78 and 6.97 (m, 4, H_{aryl}), 4.05 (t, 2, OCH_2-), plus resonances analogous to those in starting materials.

Coupling of $(EtO)_2P(O)CH_2C_6H_4CH{=}CHC_6H_5$ and 4-[4-(5-norbornenylmethoxy)-butoxy]benzaldehyde to give 6a. A solution of $(EtO)_2P(O)CH_2C_6H_4CH{=}CHC_6H_5$ (2.31 g, 7.00 mmol) in 30 mL of THF was added to a solution of KO-t-Bu (1.57 g, 14.0 mmol) in 10 mL of THF and the mixture was stirred for 30 min. A solution of 4-[4-(5-norbornenylmethoxy)butoxy]benzaldehyde (2.11 g, 7.00 mmol) in 10 mL of THF was added to this dark-red solution . The mixture was refluxed for 2h and worked up with water to precipitate solid product. Pure **6a** (3.01 g, 90%) was recrystallized from hot THF as a yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.55-7.20 and 7.05-6.85 (m, 13, H_{aryl}), 7.08 (s, 4, H_{vinyl}), 6.73 (s, 2, H_{aryl}), 6.72 (s, 2, H_{aryl}), 3.97 (t, 2, -CH_2O), plus resonances analogous to those in starting materials; λ_{max}= 372 nm (in THF). Anal. Calcd for $C_{40}H_{48}O_7$: C, 85.67; H, 7.61. Found: C, 85.43; H, 7.74.

Synthesis of 6b; $H_3C(CH_2)_5OC_6H_4CH_3$. *p*-Cresol (10.8 g, 100 mmol), 1-bromohexane (16.5 g, 100 mmol) and K_2CO_3 (15.2 g, 110 mmol) were mixed in 200 mL of DMF and the mixture was refluxed for 29h. The reaction was worked up with 400 mL of 10% NaOH solution and the product was extracted into Et_2O. The ether extract was dried over $MgSO_4$ and passed through an activated silica gel column in order to remove any trace of *p*-cresol. Pure $H_3C(CH_2)_5OC_6H_4CH_3$ (8.52 g, 44%) was obtained by vacuum distillation at 81 ± 1°C / 0.1 torr: ^{1}H NMR ($CDCl_3$) δ 6.93 (dd, 4, H_{aryl}), 3.92 (t, 2, OCH_2-), 2.28 (s, 3, CH_3), plus resonances in the 1.82-0.88 ppm region for the hexyl group.

$H_3C(CH_2)_5OC_6H_4CH_2Br$. $H_3C(CH_2)_5OC_6H_4CH_3$ (18.5 g, 44.3 mmol) and NBS (8.8 g, 48.7 mmol) were refluxed for 18h in 60 mL of CCl_4 containing a catalytic amount of AIBN. The reaction was cooled to room temperature and worked up with water. The product was extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and the solvent was removed in vacuo to give the crude product. Colorless $H_3C(CH_2)_5OC_6H_4CH_2Br$

(9.31 g , 77%) was obtained by vacuum distillation (109 ± 1°C / 0.1 torr): ^{1}H NMR ($CDCl_3$) δ 7.05(dd, 4, H_{aryl}), 4.49 (s, 2, CH_2Br), 3.92 (t, 2, OCH_2-), plus resonances in the 1.82-0.88 ppm region for the hexyl group.

$H_3C(CH_2)_5OC_6H_4CH_2P(O)(OEt)_2$. $H_3C(CH_2)_5OC_6H_4CH_2Br$ (8.00 g, 29.5 mmol) and triethyl phosphite (5.63 g, 33.9 mmol) were mixed and heated at 100°C for 5h while removing ethyl bromide in a Dean-Stark trap. Excess triethyl phosphite was removed in vacuo to give colorless product $H_3C(CH_2)_5OC_6H_4CH_2P(O)(OEt)_2$ (9.69 g, 100%): ^{1}H NMR ($CDCl_3$) δ 7.20-6.85 (m, 4, H_{aryl}), 3.96 (m, 4, $POCH_2$-), 3.88 (t, 2, OCH_2-), 3.04 (d, 2, CH_2P), plus resonances in the 1.82-0.88 ppm region for the hexyl group.

$H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4CH_3$. $H_3C(CH_2)_5OC_6H_4CH_2P(O)(OEt)_2$ (4.80 g, 14.6 mmol) and *p*-tolualdehyde (1.76 g, 14.6 mmol) were added to a suspension of NaH (80% dispersion in mineral oil, 0.66 g, 21.9 mmol) in a mixture of 100 mL of THF and 20 mL of DMF and the mixture was refluxed for 4h. The reaction was worked up with ice-water to precipitate solid product, which was dissolved in THF and reprecipitated from methanol to give pure product $H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4CH_3$ (2.92 g, 68%): ^{1}H NMR ($CDCl_3$) δ 7.45-6.82 (m, 10, H_{aryl} and H_{vinyl}), 3.95 (t, 2, OCH_2-), 2.33 (s, 3, CH_3), plus resonances in the 1.82-0.88 ppm region for the hexyl group.

$H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4CH_2Br$. A mixture containing $H_3C(CH_2)_5OC_6H_4$-$CH=CHC_6H_4CH_3$ (2.29 g, 9.92 mmol), NBS (2.03 g, 11.4 mmol), and a catalytic amount of AIBN in 80 mL of CCl_4 was refluxed for 5h. The reaction was cooled to room temperature and worked up with water. The product was extracted into $CHCl_3$. The $CHCl_3$ extract was dried over $MgSO_4$ and the solvent was removed in vacuo to give crude solid product. The product was dissolved in THF and precipitated by addition of this solution into hexane to give pure $H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4CH_2Br$ (2.12 g, 57%): ^{1}H NMR ($CDCl_3$) δ 7.50-6.80 (m, 10, H_{aryl} and H_{vinyl}), 4.50 (s, 2, CH_2Br), 3.95 (t, OCH_2-), plus resonances in the 1.82-0.88 ppm region for the hexyl group.

$H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4CH_2P(O)(OEt)_2$. $H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4$-$CH_2Br$ (2.12 g, 5.68 mmol) and triethyl phosphite(4.45 g, 26.7 mmol) were dissolved in 20 mL of toluene and the mixture was heated at 100°C for 17h. Solvent and excess triethyl phosphite were removed in vacuo to give 2.54 g (100%) of $H_3C(CH_2)_5O$-$C_6H_4CH=CHC_6H_4CH_2P(O)(OEt)_2$: ^1H NMR ($CDCl_3$) δ 7.51-6.82 (m, 10, H_{aryl} and H_{vinyl}), 4.05-3.90 (m, 4, CH_2 and OCH_2-), 3.12 (d, 2, CH_2P), plus hexyl resonances in the 1.82-0.88 ppm region.

Coupling of $H_3C(CH_2)_5OC_6H_4CH=CHC_6H_4CH_2P(O)(OEt)_2$ and 4-[4-(5-norbornenylmethoxy)butoxy]benzaldehyde to give 6b. $H_3C(CH_2)_5OC_6H_4CH=CH$-$C_6H_4CH_2P(O)(OEt)_2$ (2.45 g, 5.68 mmol) and 4-[4-(5-norbornenylmethoxy)butoxy]-benzaldehyde (1.71 g, 5.68 mmol) were added to a suspension of NaH (1.70 g, 56.8 mmol) in a mixture of 80 mL of THF and 10 mL of DMF and the mixture was refluxed for 6h. Dihydrogen was generated and yellow product (**6b**, 3.13 g, 95%) precipitated as the reaction proceeded.

Synthesis of 6c; $(EtO)_2P(O)CH_2C_6H_4CMe_3$. 4-*t*-Butylbenzyl bromide (10.0 g, 44.0 mmol) and triethyl phosphite (10.97 g, 66.0 mmol) were mixed and the mixture was heated at 100°C for 10h; ethyl bromide was removed in a Dean-Stark trap. Excess triethyl phosphite was removed in vacuo to give colorless $(EtO)_2P(O)CH_2C_6H_4CMe_3$ (12.44 g, 99%) that was pure enough to be used in the next step: ^1H NMR ($CDCl_3$) δ 7.33-7.15 (m, 4, H_{aryl}), 3.98 (m, 4, OCH_2-), 3.08 (d, 2, CH_2P), 1.26 (s, 9, CMe_3), 1.21 (t, 6, CH_3).

$(EtO)_2P(O)CH_2C_6H_4CMe_3$. $(EtO)_2P(O)CH_2C_6H_4CMe_3$ (7.05 g, 25.0 mmol) and *p*-tolualdehyde (3.1 g, 25.0 mmol) were added to a suspension of NaH (80% dispersion in mineral oil, 0.89 g, 30.0 mmol) in a mixture of 50 mL of THF and 10 mL of DMF and the mixture was refluxed for 2h. The color changed to orange-red and finally to red-purple. The mixture was worked up with water, the organic layer was extracted into Et_2O, and the extract was dried over $MgSO_4$. The solvents were removed in vacuo to

give the crude product, which was recrystallized from ether to give pure $CH_3C_6H_4CH=CHC_6H_4CMe_3$ (4.72 g, 75%): ^1H NMR ($CDCl_3$) δ 7.5-7.12 (m, 8, H_{aryl}), 7.05 (s, 2, H_{vinyl}), 2.47 (s, 3, CH_3), 1.33 (s, 9, CMe_3).

$BrCH_2C_6H_4CH=CHC_6H_4CMe_3$. $CH_3C_6H_4CH=CHC_6H_4CMe_3$ (4.72 g, 19.0 mmol) and N-bromosuccinimide (3.74 g, 21.0 mmol) were refluxed for 3h in 60 mL of CCl_4 with a catalytic amount of AIBN. The reaction mixture was cooled to room temperature, worked up with water, and extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and the solvent was removed to give crude solid product. The crude product was rinsed with Et_2O, leaving pure $BrCH_2C_6H_4CH=CHC_6H_4CMe_3$ (3.96 g, 63%) behind: ^1H NMR ($CDCl_3$) δ 7.52-7.35 (m, 8, H_{aryl}), 7.06 (m, 2, H_{vinyl}), 4.50 (s, 2, CH_2Br), 1.33 (s, 9, CMe_3).

$(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_4CMe_3$. $BrCH_2C_6H_4CH=CHC_6H_4$-CMe_3 (3.45 g, 10.5 mmol) and triethyl phosphite (2.61 g, 15.7 mmol) were dissolved in 50 mL of toluene and the mixture was heated at 100°C for 17h. Solvent and excess triethyl phosphite were removed in vacuo to give 4.00 g (99%) of $(EtO)_2P(O)CH_2$-$C_6H_4CH=CHC_6H_4CMe_3$: ^1H NMR ($CDCl_3$) δ 7.50-7.23 (m, 8, H_{aryl}), 7.03 (m, 2, H_{vinyl}), 4.00 (m, 4, OCH_2-), 3.14 (d, 2, CH_2P), 1.34 (s, 9, CMe_3), 1.24 (t, 6, CH_3).

4-(5-Norbornenylmethoxy)benzaldehyde. 5-Tosylmethyl-2-norbornene (11.1 g, 39.9 mmol) and 4-hydroxybenzaldehyde (5.11 g, 41.9 mmol) were dissolved in 150 mL of DMF containing K_2CO_3 (5.79 g, 41.9 mmol), and the mixture was refluxed for 18h. The reaction was worked up with 100 mL of water and the product was extracted into Et_2O. The extract was dried over $MgSO_4$. Column chromatography (silica gel, Et_2O/hexane = 1/4) gave 6.79 g (76%) of pure 4-(5-norbornenylmethoxy)benzaldehyde as a yellow liquid: ^1H NMR ($CDCl_3$) δ 9.85(s, 1, CHO), 7.79 and 6.94 (m, 4, H_{aryl}), 6.05 (m, 2, norbornene double bond protons), plus resonances in the 4.2-0.5 ppm region that are similar to those in the starting material.

Coupling of $(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_4CMe_3$ and 4-(5-norbornenyl-methoxy)benzaldehyde to give 6c. $(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_4CMe_3$ (4.00 g, 10.4 mmol) and 4-(5-norbornenylmethoxy)benzaldehyde (2.37 g, 10.4 mmol) were added to a suspension of NaH (0.468 g, 15.6 mmol) in a mixture of 80 mL of THF and 20 mL of DMF and the mixture was refluxed for 6h. Dihydrogen was generated and green-yellow product (**6c**, 4.21 g, 88%) formed as the reaction proceeded.

$MeC_6H_4CH_2P(O)(OEt)_2$ (7). α-Bromoxylene (10 g, 54 mmol) was mixed with triethyl phosphite(13 g, 81 mmol) and the mixture was heated at 100°C for 12h while removing EtBr in a Dean-Stark trap. Residual EtBr and excess $P(OEt)_3$ were removed in vacuo. Vacuum distillation at 105 - 106°C (0.3 torr) gave 12.66 g (97%) of pure **7**: ^1H NMR ($CDCl_3$) δ 7.10 (m,4, H_{aryl}), 3.95 (m, 4, OCH_2), 3.08 (2, CH_2P), 2.28(d, 3, $PhCH_3$), 1.2 (t, 6, CH_3).

$MeC_6H_4CH=CHC_6H_2(OMe)_3$ (8). The mixture of $MeC_6H_4CH_2P(O)(OEt)_2$ (5.0 g, 21 mmol) and 3,4,5-trimethoxybenzaldehyde (4.3 g, 22 mmol) in 5 mL of THF was added to a suspension of NaH (0.73 g, 80%, 24 mmol) in 50 mL of THF/DMF (4/1). The mixture was refluxed for 11h and worked up with ice-water. The product was extracted into Et_2O and the extract was dried over $MgSO_4$. The ether was removed in vacuo to give 4.86 g (81%) of pale-yellow solid. Pure product was obtained by recrystallization from $CHCl_3$: ^1H NMR ($CDCl_3$) δ 7.25 (dd, 4, H_{aryl}), 6.97 (s, 2, H_{vinyl}), 6.70 (s, 2, H_{aryl}), 3.90 (s, 6, O*Me*), 3.85 (s, 3, O*Me*), 2.35 (s, CH_3).

$BrCH_2C_6H_4CH=CHC_6H_2(OMe)_3$ (9). A mixture of $MeC_6H_4CH=CHC_6H_2$-$(OMe)_3$ (1.8 g, 6.4 mmol) and N-bromosuccinimide (1.3 g, 7.0 mmol) was refluxed for 13h in the presence of a catalytic amount of AIBN (32 mg, 0.22 mmol). The reaction was worked up with water and product was extracted into $CHCl_3$. The solvent was removed from the extract in vacuo to give viscous oily liquid. Trituration of the oil with ether gave 1.53 g (66%) of pale yellow solid product: ^1H NMR ($CDCl_3$) δ 7.42 (dd, 4, H_{aryl}), 7.0 (m, 2, H_{vinyl}), 6.72 (s, 2, H_{aryl}), 4.5 (s, 2, CH_2Br), 3.90 (s, 6, O*Me*), 3.85 (s, 3,

O*Me*).

$(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_2(OMe)_3$ (10). 1.53 g (4.20 mmol) of $BrCH_2C_6H_4CH=CHC_6H_2(OMe)_3$ and 1.40 g (8.40 mmol) of $P(OEt)_3$ were dissolved in 50 mL of toluene and the mixture was refluxed for 15h. (EtBr was removed in a Dean-Stark trap.) Residual EtBr and excess $P(OEt)_3$ were removed in vacuo. Pure product was obtained by recrystallizing the crude product from Et_2O by adding pentane; yield 1.30 g (73%): ^1H NMR ($CDCl_3$) δ 7.35 (m, 4, H_{aryl}), 6.98 (m, 2, H_{vinyl}), 6.71 (s, 2, H_{aryl}), 4.0 (m, 4, O*C*H_2), 3.9 (s, 6, O*Me*), 3.85 (s, 3, O*Me*), 3.25 (d, 2, *C*H_2P), 1.23 (t, 6, *C*H_3).

Synthesis of 6d; 4-(5-Norbornenylmethoxy)-3,5-dimethoxybenzaldehyde. 5-Tosylmethyl-2-norbornene (6.71 g, 24.1 mmol) and syringaldehyde (4.83 g, 26.5 mmol) were dissolved in 100 mL of DMF containing K_2CO_3 (3.66 g, 26.5 mmol), and the 0 mmol) in 3 mL of THF was added to this dark-red solution. The mixture was refluxed for 10h and worked up with water. The product was extracted into Et_2O and the extract was dried over $MgSO_4$. The solvent was removed from the extract in vacuo to give 0.92 g (53%) of product which was recrystallized from Et_2O by addition of pentane: ^1H NMR ($CDCl_3$) δ 7.48 (s, 4, center H_{aryl}), 7.01 (m, 4, H_{vinyl}), 6.73 (s, 2, side H_{aryl}), 6.72 (s, 2, side H_{aryl}), 3.91 (s, 6, O*Me*), 3.89 (s, 6, O*Me*), 3.86 (s, 3, O*Me*), plus resonances analogous to those in starting materials; λ_{max}= 372 nm (in THF).

4-[5-(5-Norbornenylmethoxy)pentoxy]-3,5-dimethoxybenzaldehyde (11). A mixture of 5-(5-norbornenylmethoxy)pentyl bromide (5.7 g, 21 mmol) and syringaldehyde (3.8 g, 21 mmol) was heated at 80°C for 60h in the presence of K_2CO_3 (4.3 g, 31 mmol). The mixture was worked up with water and the product was extracted into Et_2O. The product (2.03 g, 26%) was separated by column chromatography (silica gel, Et_2O/pentane = 1/1): ^1H NMR ($CDCl_3$) δ 9.85 (s, 1, C*H*O), 7.10 (s, 2, H_{aryl}), 3.78 (s, 6, O*Me*), plus resonances similar to those in the starting materials.

NBTPV-C_5 (6e). $(EtO)_2P(O)CH_2C_6H_4CH=CHC_6H_2(OMe)_3$ (1.00 g, 2.40 mmol) in 20 mL of THF was added to a solution of KO-t-Bu (0.54 g, 4.80 mmol) in 10

mL of THF and the mixture was stirred for 30 min. A solution of 4-[5-(5-norbornenylmethoxy)pentoxy]-3,5-dimethoxybenzaldehyde (900 mg, 2.40 mmol) in 3 mL of THF was added to this dark-red solution. The mixture was refluxed for 15h and worked up with water. The product was extracted into Et_2O and the extract was dried over $MgSO_4$. The solvent was removed from the extract in vacuo to give 0.67 g (44%) of product which was recrystallized from THF by addition of pentane: ^1H NMR ($CDCl_3$) δ 7.48 (s, 4, center H_{aryl}), 7.10 (m, 4, H_{vinyl}), 6.73 (s, 2, side H_{aryl}), 6.72 (s, 2, side H_{aryl}), 3.97 (t, 2, -C*H*$_2$O), 3.91 (s, 6, O*Me*), 3.88 (s, 6, O*Me*), 3.86 (s, 3, O*Me*), plus resonances analogous to those in starting materials; λ_{max}= 372 nm (in THF). Anal. Calcd for $C_{40}H_{48}O_7$: C, 74.97; H, 7.55. Found: C, 74.56; H, 7.54.

Polymerization of NBTPV-C_5 (6e). A solution of Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ (400 μL of the stock solution of 10 mg in 2000 μL of THF; 3.64 μmol) was added quickly to a solution of NBTPV-C_5 (117 mg, 182 μmol) in 5 mL of THF . After 3h benzaldehyde (3.8 μL, 36 μmol) was added and 1 hour later the polymer was precipitated by adding the polymer solution into pentane; yield 95%, PDI = 1.10 in THF versus polystyrene standards: $\lambda_{max,abs}$ = 368 nm (in THF) and 362 nm (cast film), $\lambda_{max,em}$ = 475 nm (cast film).

9,10-Diphenylanthracene (DPA, 13). 50 mL of PhMgCl (3.0M solution, 150 mmol) was slowly added over a period of 1h to the boiling solution of anthraquinone (10.4 g, 50 mmol) in 150 mL of benzene. The mixture was refluxed for 18h, worked up with ice-water (orange solution with lots of salt), and acidified with 15 mL of 6N HCl (clear yellow solution). The organic layer was separated and dried over $MgSO_4$. Solvent was removed in vacuo and the resulting sticky material was rinsed with Et_2O to give off-white solid. After rinsing the solid with hot acetone, no more starting material was detected by NMR and 10.58 g (58%) of 9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene was collected: ^1H NMR ($CDCl_3$) δ 7.55-7.20 (m, 18, H_{aryl}), 2.68 (s, 2, O*H*).

9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (3.75 g, 10.3 mmol), KI (5.15 g, 31.0 mmol) and NaH_2PO_2 (9.94 g, 113 mmol) were mixed in 60 mL of acetic acid and the mixture was heated at 80°C for 3.5h. The mixture was diluted with 400 mL of water, and the solid product was filtered off and rinsed with cold EtOH (3.03 g, 89%): ^{1}H NMR ($CDCl_3$) δ 7.73-7.28 (m, 18, H_{aryl}).

CH_3CO-DPA (14). Acetyl chloride (0.94 g, 12.6 mmol) was added to a suspension of $AlCl_3$ (1.76g, 13.2 mmol) in 10 mL of CH_2Cl_2. This mixture was added to the solution of DPA (3.96 g, 12.0 mmol) in 60 mL of CH_2Cl_2. The mixture was stirred for 24h and worked up with ice. The organic layer was separated and dried over $MgSO_4$. The solvent was removed and the product (3.17 g, 77%) was separated by column chromatography (silica gel, $CHCl_3$/hexane = 2/1): ^{1}H NMR ($CDCl_3$) δ 8.35-76.30 (m, 17, H_{aryl}), 2.47 (s, 3, $COCH_3$)

$CH_3(HO)CH$-DPA (15). A solution of CH_3CO-DPA (5.23 g, 15.2 mmol) in 30 mL of THF was added to a solution of $NaBH_4$ (1.15 g, 30.4 mmol) in 15 mL of EtOH and the mixture was stirred for 4h. The mixture was worked up with water and acidified with 1.0M HCl until pH = 5.0. The product was extracted into Et_2O. Solvent was removed in vacuo and the residue was separated by column chromatography (silica gel, Et_2O/hexane = 1/1) to give a product (4.36 g, 83%): ^{1}H NMR ($CDCl_3$) δ 7.72-7.27 (m, 17, H_{aryl}), 4.90 (q,1, CH), 1.73 (s, 1, OH), 1.25 (d, 2, CH_3).

2-Methyl-9,10-diphenylanthracene (16). PhMgCl solution (68 mL, 3.0M solution, 202 mmol) was slowly added over a period of 30 min to a boiling solution of 2-methylanthraquinone (10.0 g, 45.0 mmol) and the mixture was refluxed for 3h. The mixture was worked up with saturated NH_4Cl solution. The organic layer was separated and dried over $MgSO_4$. After solvent was removed in vacuo, the resulting sticky material was dissolved in THF and precipitated into hexane to give off-white 9,10-dihydroxy-9,10-diphenyl-2-methyl-9,10-dihydroanthracene (9.10 g, 54%): ^{1}H NMR ($CDCl_3$) δ 7.50-7.00 (m, 17, H_{aryl}), 2.63 (s, 1, OH), 2.57 (s, 1, OH), 2.22 (s, 3, CH_3).

9,10-Dihydroxy-9,10-diphenyl-2-methyl-9,10-dihydroanthracene (9.10 g, 24.0 mmol), KI (11.95 g, 72.0 mmol) and NaH_2PO_2 (23.23 g, 264 mmol) were mixed in 100 mL of acetic acid and the mixture was heated at 80°C for 4h. The mixture was diluted with 500 mL of water. The solid product (light brown color) was filtered off and rinsed with cold EtOH (8.02 g, 97%). Pure product (7.6 g, 92%) was obtained as a pale yellow solid by sublimation (120°C/0.01 torr): ^{1}H NMR ($CDCl_3$) δ 7.70-7.12 (m, 17, H_{aryl}), 2.47 (s, 3, CH_3).

DPA-CH_2CO_2H (17). To a precooled (-30°C) solution of Me-DPA (0.50 g, 1.45 mmol) in 15 mL of THF was added a mixed solution of *n*-BuLi (2.54M, 1.2 mL, 3.04 mmol) and TMEDA (0.18 g, 1.52 mmol). The mixture was warmed to room temperature, stirred for 1h and poured into crushed dry-ice. After all the excess dry-ice was evaporated, the mixture was worked up with 1M HCl and the product was extracted into THF. The extract was dried over $MgSO_4$. Solvent was removed in vacuo and the residue was separated by column chromatography (silica gel, $CHCl_3/Et_2O$ = 9/1) to give 0.32 g (57%) of yellow product: ^{1}H NMR ($CDCl_3$) δ 7.70-7.22 (m, 17, H_{aryl}), 3.67 (s, 2, CH_2), 1.25 (s, 1, CO_2H).

DPA-CH_2CH_2OH (18). A solution of DPA-CH_2CO_2H (0.82 g, 2.10 mmol) in 10 mL of THF was added to a suspension of $LiAlH_4$ (160 mg, 4.20 mmol) in 30 mL of THF and the mixture was stirred for 3h. The reaction mixture was treated with water and the product was extracted into Et_2O. The extract was dried over $MgSO_4$ and the solvent was removed in vacuo to give 0.78 g (100%) of product: ^{1}H NMR ($CDCl_3$) δ 7.70-7.20 (m, 17, H_{aryl}), 3.83 (t, 2, CH_2), 2.88 (t, 2, CH_2), 1.62 (s, 1, OH).

Carbo-2-[2-(9,10-diphenylanthracenyl)]ethoxynorbornene (19). DPA-CH_2CH_2OH (1.00 g, 2.7 mmol) and Et_3N (0.27 g, 2.7 mmol) were mixed in 10 mL of THF. The mixture was added to a solution of norbornenecarbonyl chloride (0.42 g, 2.7 mmol) in 15 mL of THF and stirred for 1h. Solvent was removed in vacuo and the product was extracted into pentane. After solvent was remove in vacuo, yellow solid

(1.22 g) was obtained. This product was not pure and many efforts to purify were unsuccessful.

2-[4-(5-Norbornenylmethoxy)butoxy]-6-hydroxy-9,10-anthraquinone (20). 2,6-Dihydroxy-9,10-anthraquinone (5.56 g, 23.1 mmol), 5-(4-bromobutoxy)methyl-norbornene (3.00 g, 11.6 mmol) and K_2CO_3 (3.20 g, 23.1 mmol) were mixed in 150 mL of DMF and the mixture was heated at 60°C for 20h. The reaction mixture was worked up with water and the product was extracted into Et_2O. The extract was rinsed with water until the aqueous layer was colorless and dried over $MgSO_4$. After solvent was removed in vacuo, the residue was redissolved in THF and precipitated into hexane to give yellow precipitate. Green-brown product (3.5 g, 72%) was obtained after vacuum dry: ^{1}H NMR (DMSO-d_6) δ 10.98 (s, 1, O*H*), 8.25 (t, 2, H_{aryl}), 7.44 (dd, 2, H_{aryl}), 7.27 (dd, 1, H_{aryl}), 7.19 (dd, 1, H_{aryl}), 6.13-5.85 (m, 2, H_{vinyl}), 4.18 (t, 2, -C*H*$_2$O), plus resonances in the 3.5-0.3 ppm region that are similar to those in the starting material.

2-[4-(5-Norbornenylmethoxy)butoxy]-6-methoxy-9,10-anthraquinone (21). A solution of 2-[4-(5-norbornenylmethoxy)butoxy]-6-hydroxy-9,10-anthraquinone (3.50 g, 8.36 mmol) in 15 mL of DMSO was added to a crushed KOH suspension in 30 mL of DMSO to generate dark-red solution. The solution of CH_3I (2.37 g, 16.7 mmol) in 10 mL of DMSO was added to this dark-red solution and the mixture was stirred for 18h. The reaction mixture was worked up with water and extracted with THF. The organic layer was acidified with 50 mL of 0.5M HCl, washed with water several times, and dried over $MgSO_4$. The solvent was removed from the extract in vacuo to give viscous yellow solid. Recrystallization from THF layered with hexane gave 3.0 g (83%) of pure product: ^{1}H NMR ($CDCl_3$) δ 8.20 (dd, 2, H_{aryl}), 7.70 (dd, 2, H_{aryl}), 7.20 (dt, 2, H_{aryl}), 6.0 (m, 2, H_{vinyl}), 4.17 (t, 2, OC*H*$_2$), 3.95 (s, 3, OC*H*$_3$), plus resonances in the 3.5-0.3 ppm region that are similar to those in the starting material.

2-[4-(5-Norbornenylmethoxy)butoxy]-6-methoxy-9,10-dihydoxy-9,10-diphenyl-9,10-hydroanthraquinone (22). PhMgCl solution (3.0M, 5.53 mL, 16.6 mmol) was

added to a boiling solution of 2-[4-(5-norbornenylmethoxy)butoxy]-6-methoxy-9,10-anthraquinone (1.80 g, 4.16 mmol) in 50 mL of benzene . The mixture was refluxed for 17h and worked up with a saturated aqueous NH_4Cl solution. The organic layer was separated and dried over $MgSO_4$. After solvent was removed from the organic layer in vacuo, the residue was rinsed with Et_2O to give the product as a white powder (0.48 g, 20%): ^1H NMR ($CDCl_3$) δ 7.25-6.72 (m, 16, H_{aryl}), 5.95 (m, 2, H_{vinyl}), 3.65 (s, 3, OCH_3), 2.55 (s, 2, OH), plus resonances in the 3.9-0.4 ppm region that are similar to those in the starting material.

2-[4-(5-Norbornenylmethoxy)butoxy]-6-methoxy-9,10-diphenylanthracene (23). 2-[4-(2-Norbornenylmethoxy)butoxy]-6-methoxy-9,10-dihydoxy-9,10-diphenyl-9,10-hydroanthraquinone (0.48 g, 0.82 mmol), KI (0.41 g, 2.45 mmol) and NaH_2PO_2 (0.79 g, 9.00 mmol) were mixed in 10 mL of acetic acid and the mixture was heated at 80°C for 3h. The mixture was diluted with 100 mL of water. The solid product was filtered and rinsed with cold EtOH (0.39 g, 87%). Pale yellow product (0.27 g 60%) was obtained by column chromatography (silica gel, $CHCl_3$/hexane = 2/3) : ^1H NMR ($CDCl_3$) δ 7.62-7.42 (m, 12, H_{aryl}), 6.99 (ddd, 2, H_{aryl}), 6.81 (t, 2, H_{aryl}), 5.99 (m, 2, H_{vinyl}), 3.83 (t, 2, OCH_2), 3.66 (s, 3, OCH_3), plus resonances in the 3.9-0.4 ppm region that are similar to those in the starting material.

REFERENCES

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Bradley, D. D. C. *J. Phys. D: Appl. Phys* **1987**, *20*, 1389.

(3) Braun, D.; Heeger, A. J. *J. Appl. Phys. Lett.* **1991**, *58*, 1982.

(4) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.

(5) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(6) Momii, T.; Tokito, S.; Tsutsui, T.; Saito, S. *Chem. Lett.* **1988**, 1201.

(7) Tokito, S.; Momii, T.; Murata, H.; Tsutsui, T.; Saito, S. *Polymer* **1990**, *31*, 1137.

(8) Burn, P. L.; Holmes, A. B.; Kraft, A.; Brown, A. R.; Bradley, D. D. C.; Friend, R. H. *Mat. Res. Soc. Symp. Proc.* **1991**, *247*, 647.

(9) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R. F., R. H. *J. Chem. Soc. Chem. Comm.* **1992**, 32.

(10) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polymer Comm.* **1985**, *26*, 362.

(11) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.

(12) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.

(13) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. Appl. Phys.* **1991**, *30*, L1941.

(14) Bradley, D. D. C. *Chemistry in Britain* **1991**, *27*, 719.

(15) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

(16) Hudson, B. S.; Kohler, B. E.; Schuten, K. "Excited States"; Academic: New York, 1982; Vol. 6.

(17) Yan, M.; Rothberg, L. J.; Papadimitrakopoulos, F.; Galvin, M. E.; Miller, T. M.

Phys. Rev. Lett. **1994**, *72*, 1104.

(18) Samuel, I. D. W.; Crystall, B.; Rumbles, G.; Burn, P. L.; Holmes, A. B.; Friend, R. H. *Chem. Phys. Lett.* **1993**, *213*, 472.

(19) Greenham, N. C. G. *Personal Communication*

(20) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.

(21) Schrock, R. R. in "Ring-Opening Polymerization"; D. J. Brunelle, Ed.; Hanser: Munich, 1993; pp 129.

(22) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(23) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organometal. Chem.* **1993**, *459*, 185.

(24) Fox, H. H.; Schrock, R. R. *Organometallics* **1994**, *13*, 635.

(25) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Puccetti, G.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1993**, *115*, 860.

(26) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Dhenaut, C.; LeDoux, I.; Zyss, J. *Macromolecules* **1994**, *27*, 1875.

(27) Fox, H. H. Ph.D. Thesis, MIT, 1993.

(28) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(29) Campbell, T. W.; McDonald, R. N. *J. Org. Chem.* **1959**, *24*, 1246.

(30) Griffin, C. E.; Martin, K. R.; Douglas, B. E. *J. Org. Chem.* **1962**, *27*, 1627.

(31) Vollhardt, K. P. C. *Synthesis* **1975**, 765.

(32) Kosolapoff, G. M. *J. Chem. Soc.* **1944**, *66*, 109.

(33) Kosolapoff, G. M. *J. Chem. Soc.* **1944**, *66*, 1511.

(34) Wadsworth, W. S., Jr.; Emmons, W. D. *J. Chem. Soc.* **1961**, *83*, 1733.

(35) Dombrovskii, A. V.; Dombrovskii, V. A. *Russ. Chem. Rev.* **1966**, *35*, 733.

(36) Stolka, M.; Pai, D. M.; Renfer, D. S.; Yanus, J. F. *J. of Poly. Sci.: Poly. Chem. Ed.* **1983**, *21*, 969.

(37) Verbruggen, M.; Zhou, Y.; Lenstra, A. T. H.; Geise, H. *Acta. Cryst.* **1988**, *C44*, 2120.

(38) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1989**, *55*, 1489.

(39) Hamada, Y.; Adachi, C.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 1812.

(40) Schafer, F. P. "Topics in Applied Physics"; 3rd ed.; Springer-Verlag: New York, 1990.

(41) Drexhage, K. H. *Laser Focus* **1973**, *9*, 35.

(42) Tuccio, S. A.; Drexhage, K. H.; Reynolds, G. A. *Opt. Commun.* **1973**, *7*, 248.

(43) Adam, W.; Cilento, G. "Chemical and Biological Generation of Excited States."; Academic: New York, 1982.

(44) Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 139.

(45) Keszthelyi, C. P.; Bard, A. J. *J. Electrochem. Soc.* **1973**, *120*, 241.

(46) Gill, S. K. *Aldrichimica. Acta.* **1983**, *16*, 59.

(47) Jacobine, A. F.; Glaser, D. M.; Nakos, S. T. *ACS Polym. Mat. Sci. Eng* **1989**, *60*, 211.

(48) Greenham, N. C.; Friend, R. H.; Bradley, D. D. C. *Adv. Mater.* **1994**, *6*, 491.

CHAPTER 3

Photoinduced Electron Transfer in Redox-Active Block Copolymers Prepared by ROMP

INTRODUCTION

One of the most remarkable achievements of photochemistry is the recognition that certain molecules become powerful electron donors or acceptors upon photoexcitation. This phenomenon is known as photoinduced electron transfer (PET).[1] Under normal conditions where the change in energy (ΔE) accompanying the electron transfer is positive, electron transfer does not occur because the electron affinity (EA) of

$$\Delta E = IP - EA > 0$$

the acceptor does not exceed the ionization potential (IP) of the donor (Scheme 3.1). When a molecule absorbs a photon, its ionization potential may decrease and its electron affinity may increase (Koopman's theorem).[2] In both cases, the excited state may be either an electron donor (Scheme 3.1a) or an electron acceptor (Scheme 3.1b). The new ΔE ($= IP - EA - E_{00}$) becomes negative and electron transfer is feasible.

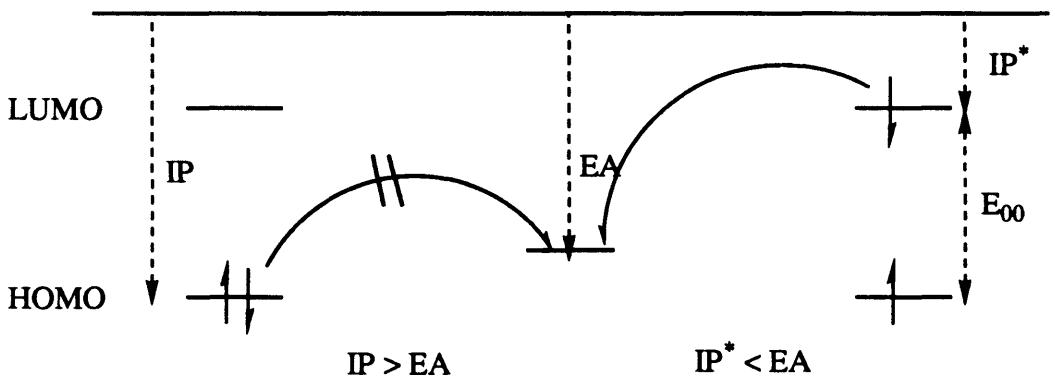
$$IP^* = IP - E_{00}$$

$$EA^* = EA + E_{00}$$

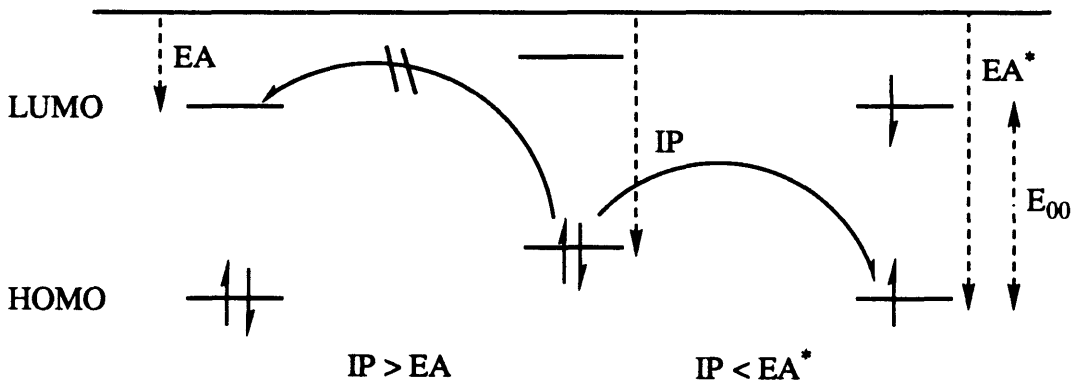
E_{00} is $0 \rightarrow 0$ electronic transition energy

Photoinduced electron transfer has attracted the interest of chemists from many fields. In organic chemistry, for example, interest in PET has uncovered novel pathways for the synthesis of organic molecules.[3,4] Inorganic chemists have applied PET to the development of solar energy storage and conversion systems, utilizing transition metal complexes.[5,6] Molecular biologists are investigating photosynthesis and electron-transport in biological systems on the basis of simple models of PET.[7] Particularly in the chemical approaches to artificial photosynthesis, the charge-separated (CS) state of radical ion pairs (Scheme 3.2) generated by PET require a reasonable lifetime to migrate the excitation energy to the active site where useful chemical reactions can occur before it decays to the ground state (back electron transfer). In most cases, however, back electron transfer has an appreciable thermodynamic driving force and diffusion-controlled charge

a) Photoexcited donor

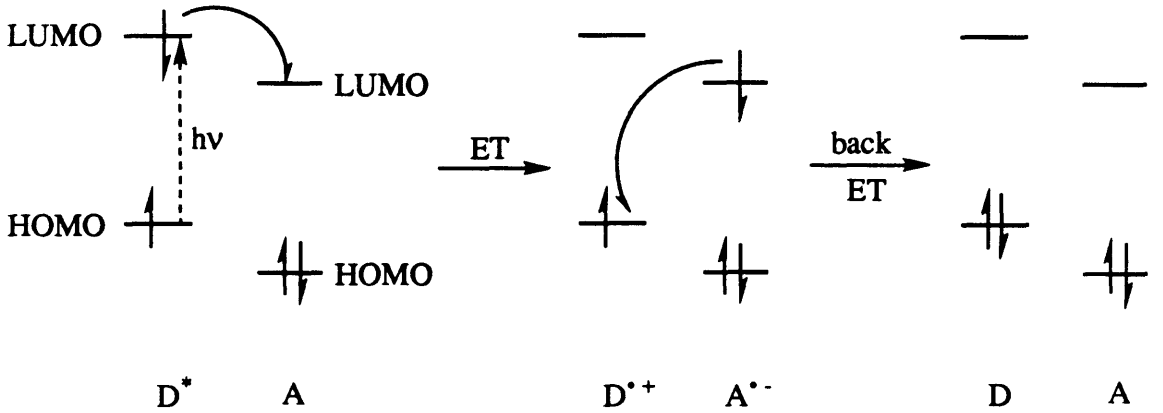


b) Photoexcited acceptor

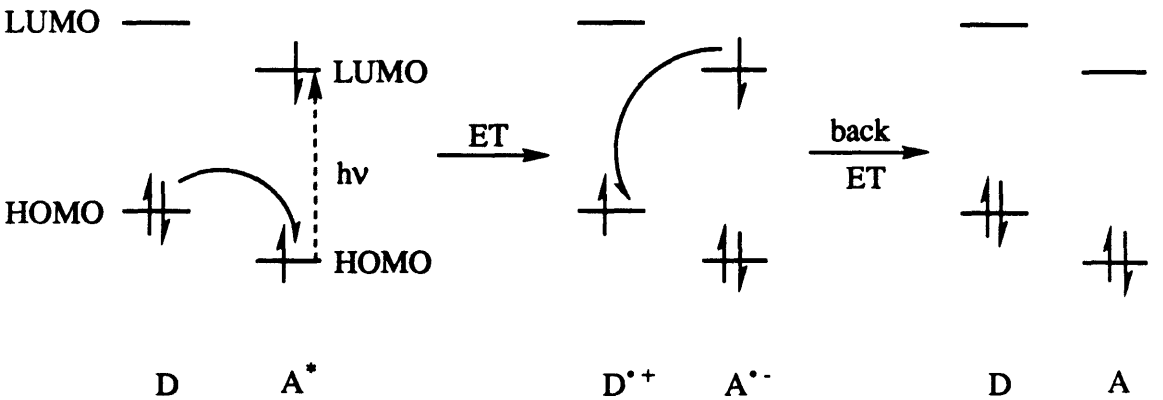


Scheme 3.1. The feasibility of PET dictated by the relative energies of (a) donor and (b) acceptor electrons.

a) Excited electron donor

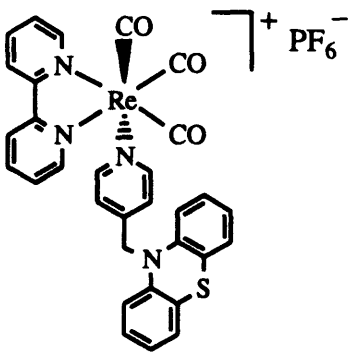


b) Excited electron acceptor



Scheme 3.2. Energetics for forward and back electron transfer for (a) an excited electron donor and (b) an excited electron acceptor.

recombination is so fast that kinetic suppression of back electron transfer often becomes the limiting factor in the ability of the chemist to observe well-defined chemistry derived from PET.[8] In order to suppress the back electron transfer, non-homogeneous media such as micelles, emulsions, or layered structures have been used[9]. A modified natural photosynthetic system in which donor and acceptor molecules are covalently attached to the opposite end of a long rigid hydrocarbon spacer has also been investigated.[10-13] An impressive model compound (molecular pentad) with two porphyrins as the chromophore, a carotenoid donor and two quinone acceptors has been synthesized and found to possess a long-lived charge separated state (τ = 55 μs) with a high quantum yield (Φ = 0.83).[14] Another model system is based on Ru and Re polypyridyl chromophores.[15] Ru and Re polypyridyl complexes are useful because their synthesis is more direct and because their lowest excited state is a metal to ligand charge transfer (MLCT) state, providing a small degree of charge separation in the initial excited state. Furthermore, the back electron transfer of charge separated state in these complexes is in the so-called Marcus inverted region[16,17] and a clear relationship between back electron transfer and nonradiative decay has been observed.[18] For example, phenothiazine-attached Re(I) polypyridyl complexes are known to have long-lived, spectroscopically identifiable charge separated states.[17-22] The linked chromophore-donor complex (**1**) was



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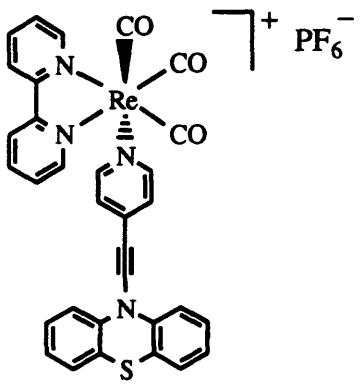


2

first made and studied by Meyer and co-workers.[19] This complex showed a long lifetime (25 ns) of charge separated (CS) state. A similar complex, **2**, which has a more rigid spacer between chromophore and donor molecule was prepared by the Wrighton group and showed a longer CS state lifetime of 31 ns.[23]

The coupling of single photon and single electron transfer events to multi-electron reactions such as the oxidation of water or the reduction of carbon dioxide is an unsolved problem in artificial photosynthesis.[8] One promising approach to solving this problem is by the synthesis of molecular assemblies containing multiple sites in order to achieve light absorption, electron/energy transfer, and multi-electron redox reaction. Soluble polymers can serve this role and a number of photochemical electron transfer assemblies based on polymers have been reported.[15,24-30] However, the conformational flexibility of organic polymers (usually substituted polystyrene or polymethyl methacrylate) has prevented successful long range energy or electron transfer because polymer folding generates eximers or exiplexes.[24,26,27,31-36] More rigid polymer systems are required to avoid e polymer assemblies.[37] Although new types of chromophore- and donor- (or acceptor-) labeled copolymers have been investigated in order to build a polymer array for directional electron or energy transfer,[38,39] these polymers are random copolymers without the controlled sequential order or size of each block. The primary structure of a polymer and its morphology can be controlled by living polymerization, but traditional living polymerization methods such as anionic, cationic, and group transfer polymerization generally do not tolerate the required redox-active groups.[40]

Recently, several well-defined electroactive and photoactive polymers have been prepared by ring opening metathesis polymerization (ROMP) and their properties studied.[41-43] ROMP has characteristic advantages for the preparation of the redox-active polymers. First, well-characterized catalysts are available with certain variety and tolerate many functionalities.[41,44] The preparation of functionalized norbornenes is easily accomplished via Diels-Alder reactions and simple coupling reactions thereafter. Since

ROMP is a living polymerization, block copolymers can be prepared from monomers that contain chromophore and quencher groups as side chains. Therefore polymer films that contain chromophores and quenchers in specific morphologies (layers, rods, spheres) can be prepared.[45] Furthermore, by choosing the appropriate catalyst and capping reagent it is possible to functionalize each end of the polymer; this strategy is useful for preparing a polymer array for directional electron or energy transfer or for attaching the polymer to an electrode surface.[21,46-48]

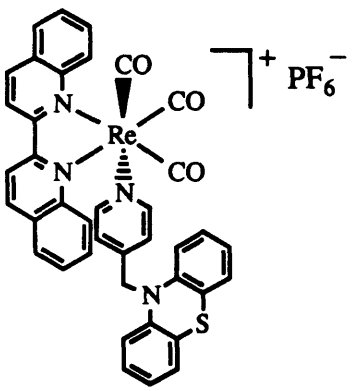
In this chapter novel types of photoactive polymers, chromophore-capped homopolymers and block copolymers of electron donors, are designed and their photophysical characterization is presented. The spectroscopy of several molecular models is examined and the concept of chain electron transfer is introduced.

The work reported in this Chapter 3 was carried out in collaboration with Drs. David Albagli, Eric J. Lee, and Xiaohong Zhao of professor Mark Wrighton's research group. A portion of the results that are described in this chapter has been included in their theses.[49,50]

RESULTS AND DISCUSSION

Chromophore-donor linked model compounds

A new phenothiazine-linked Re(I) polypyridyl complex (**3**) was prepared by Dr. David Albagli and found to generate a long-lived charge separated state (τ = 15 ns) by photoinduced electron transfer. This value was calculated from the transient absorption decay kinetics at 515 nm, which is a characteristic absorption for the oxidized phenothiazine radical cation ($PTZ^{\bullet+}$). The tetramethylphenylenediamine (TMPD) linked analog (**4**) was also prepared, which is the first example of a TMPD attached metal



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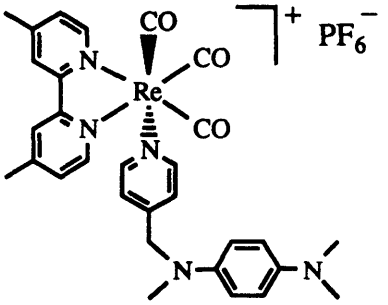


4

polypyridyl chromophore. This complex showed a slower back electron transfer rate than the rate of the forward electron transfer, and the charge separated state was accumulated for being monitored by transient absorption spectroscopy ($\tau \approx 6$ ns). The transient absorption spectrum of **4b** and the absorption decay curve at 568 nm are shown in Figure 3.1. Electrochemical and chemical oxidation of **4** were carried out in CH_3CN and absorption spectra showed exactly the same absorption pattern of $TMPD^{\bullet+}$ (Figure 3.2). The results of these chromophore-donor linked model complexes (**3** and **4**) which can generate long-lived and spectroscopically accessible charge separated states, predicts that Re chromophore-capped polymers of donor molecules are good polymeric systems for extending lifetimes of charge separated states.

In order to introduce a Re polypyridyl chromophore into the ROMP polymer, the new Re complex, $(CHO\text{-}py)(CO)_3(biq)Re^+PF_6^-$ (**5**), biq = biquinoline, was prepared from $(CH_3CN)(CO)_3(biq)Re^+PF_6^-$ and pyridinealdehyde by Dr. Eric J. Lee. This complex generated the oxidized radical cation ($Me\text{-}PTZ^{\bullet+}$) by bimolecular photoinduced electron transfer in CH_3CN solution as expected (Figure 3.3). **5** was treated with $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ in CD_2Cl_2 to give a coupled product (**6**) quantitatively (eq 3.1).

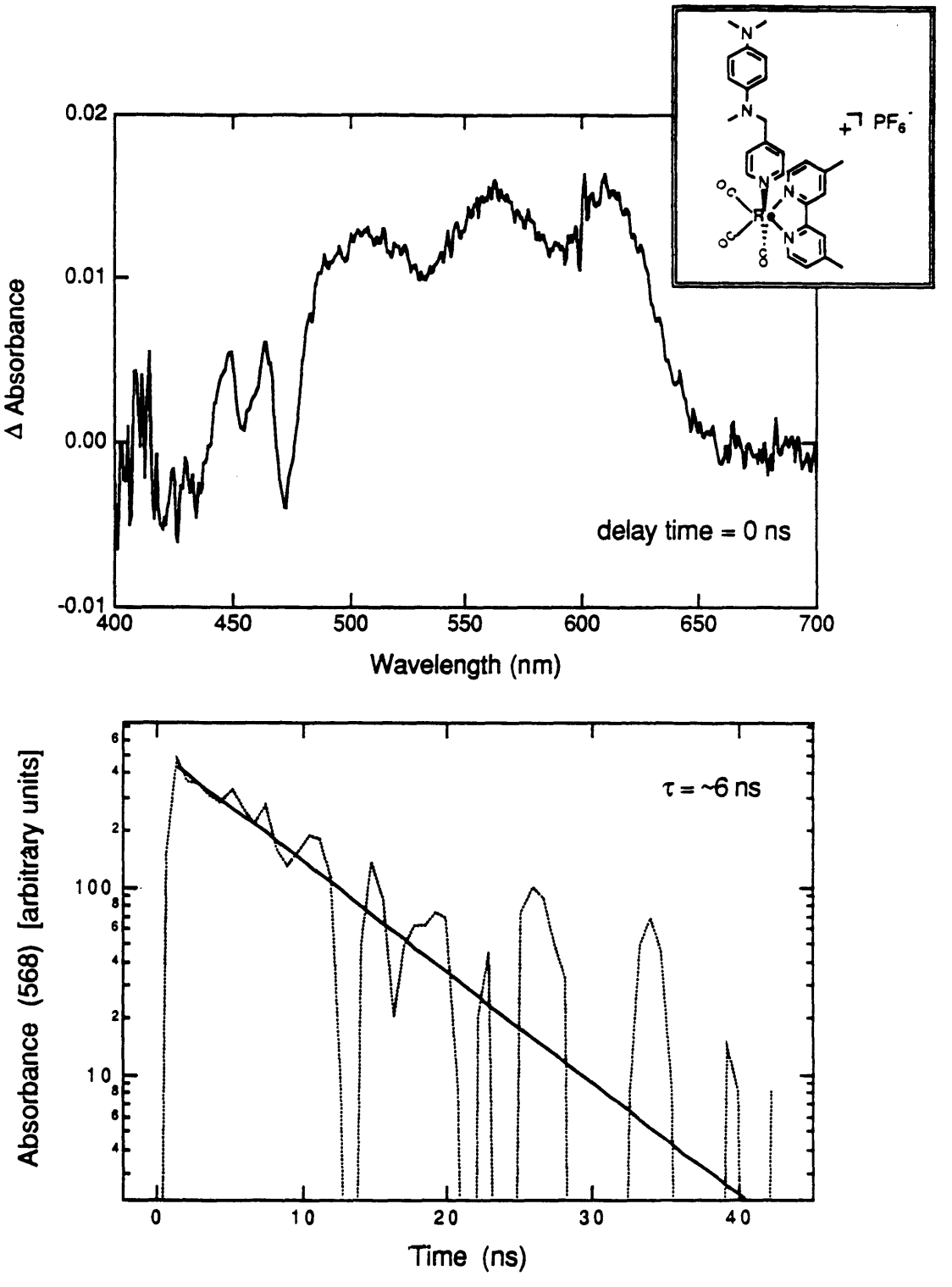
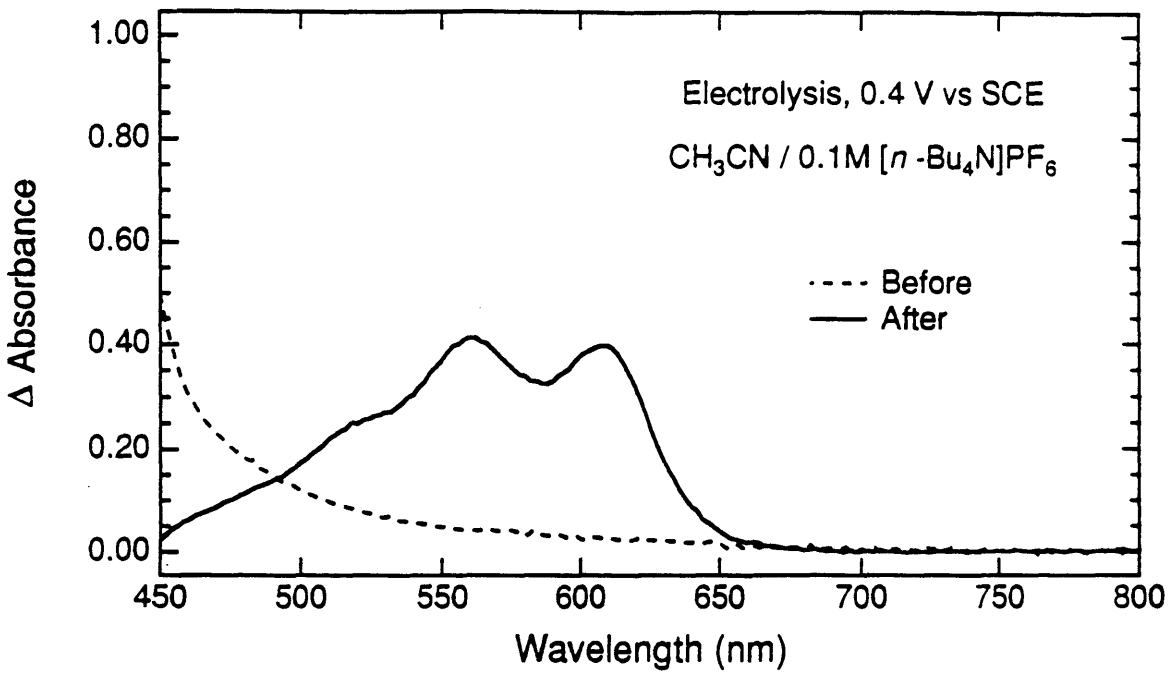


Figure 3.1. Transient absorption spectrum and absorption decay curve of Re(Me_2-py)(py-TMPD) (**4**).



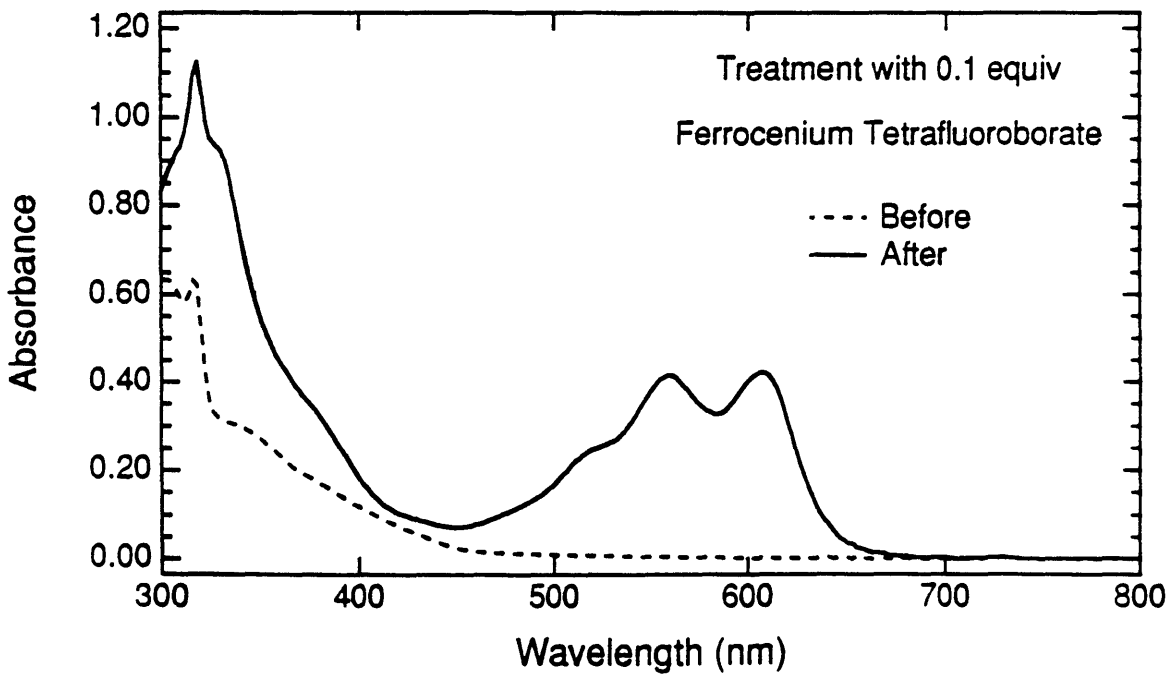


Figure 3.2. Absorption spectra of the first oxidation product of Re(Me_2-py)-(py-TMPD) (4) by electrochemical and chemical method.

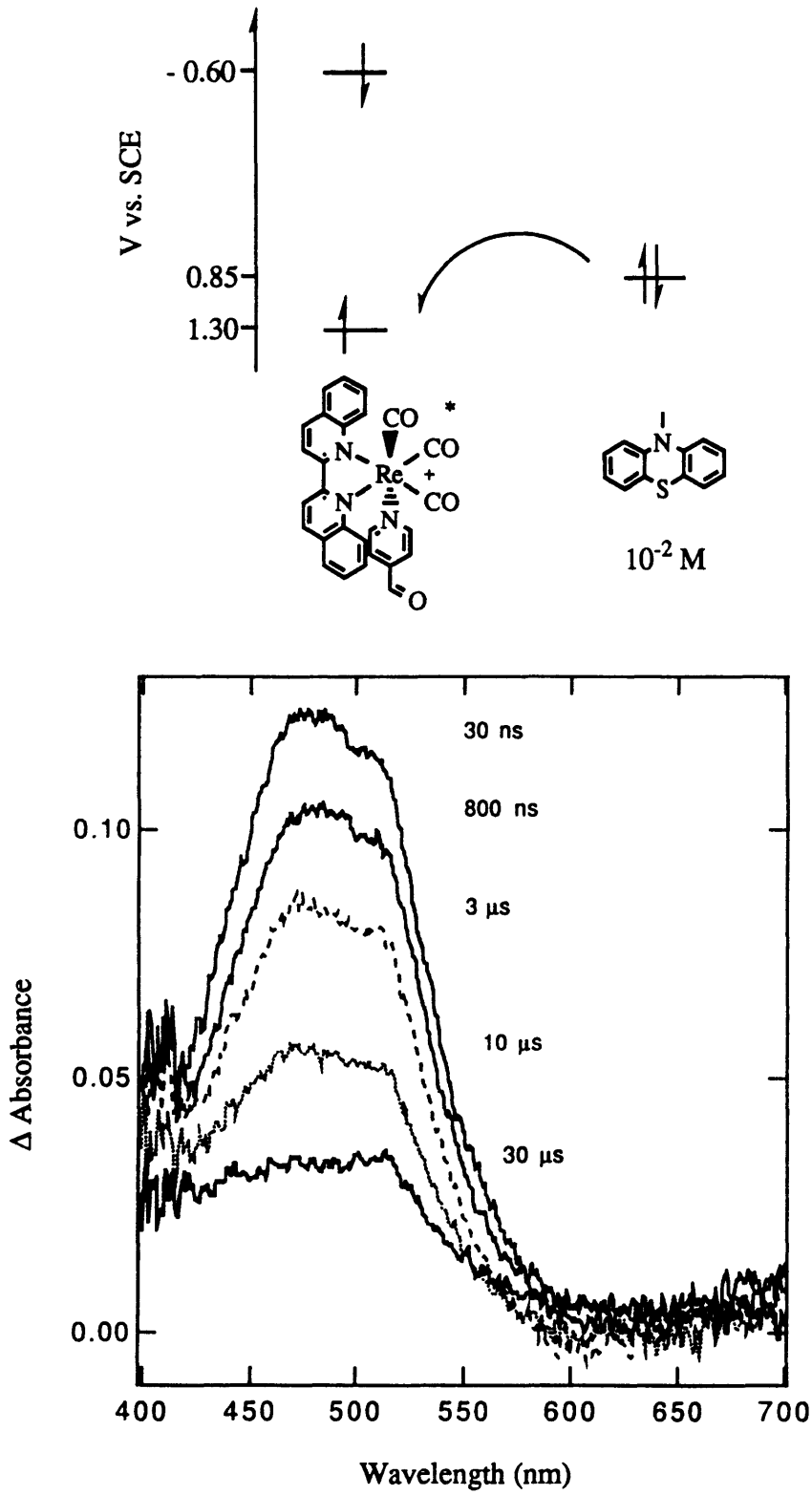
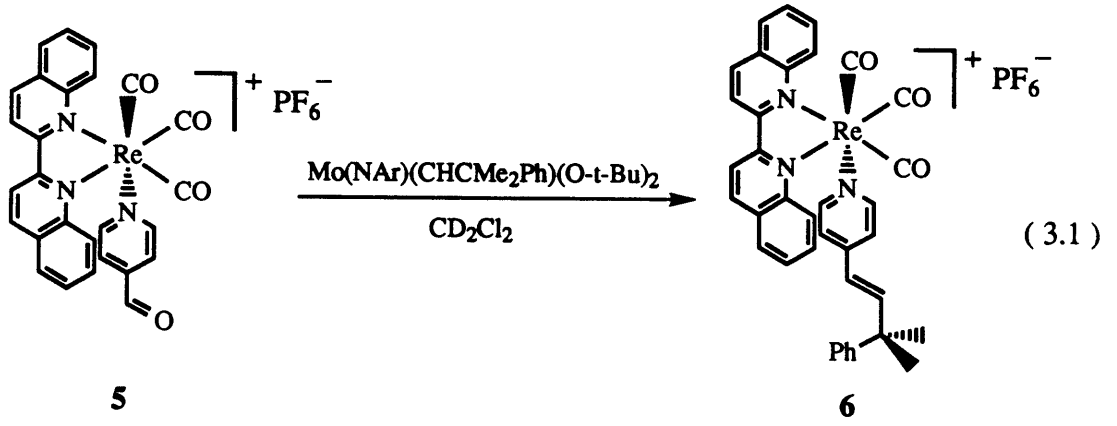
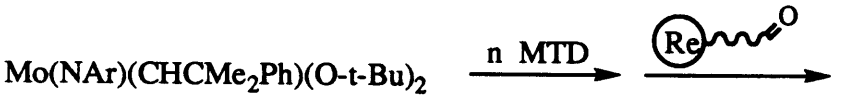


Figure 3.3. Energetics of bimolecular PET in **5** and Me-PTZ and transient absorption spectra at indicated times following 10 ns 416 nm excitation of **5**.

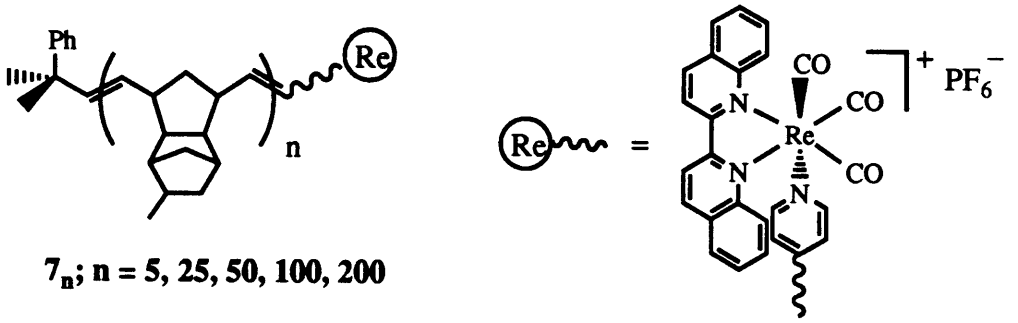


5 **6** (3.1)

Homopolymers, polyMTD, were prepared from $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ catalyst and capped with **5** to afford the corresponding Re chromophore-capped polymers (eq 3.2). The attempt to characterize the polymer by gel permeation chromatography (GPC),



(3.2)



7_n; n = 5, 25, 50, 100, 200

however, failed probably due to the ionic sites of the polymer having ionic interactions with the stationary phase of the GPC column rather than solely by size exclusion. Steady-state emission spectra of **6** and **7** showed the typical emission of Re polypyridyl complexes at 630 nm (Figure 3.4).

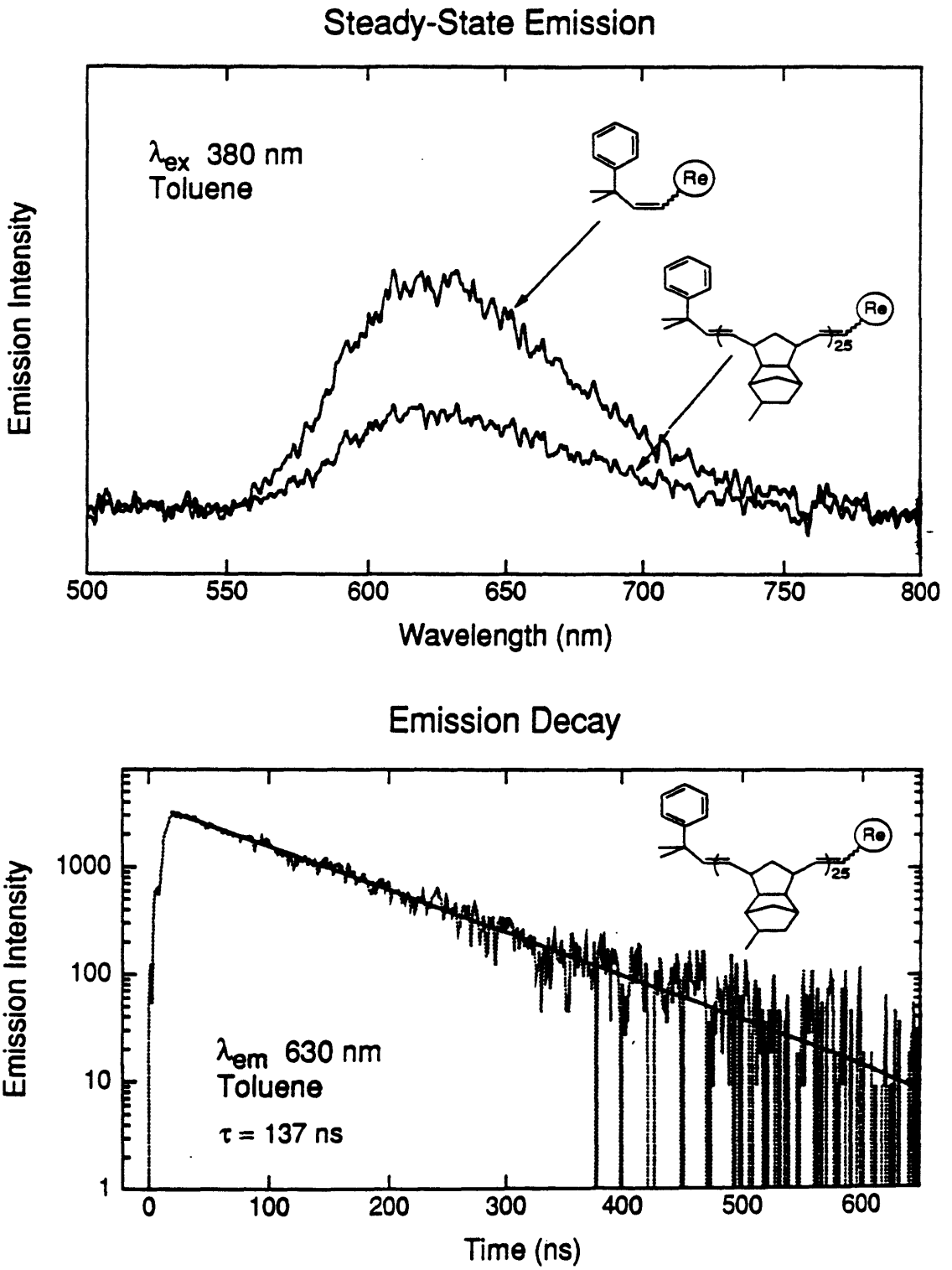
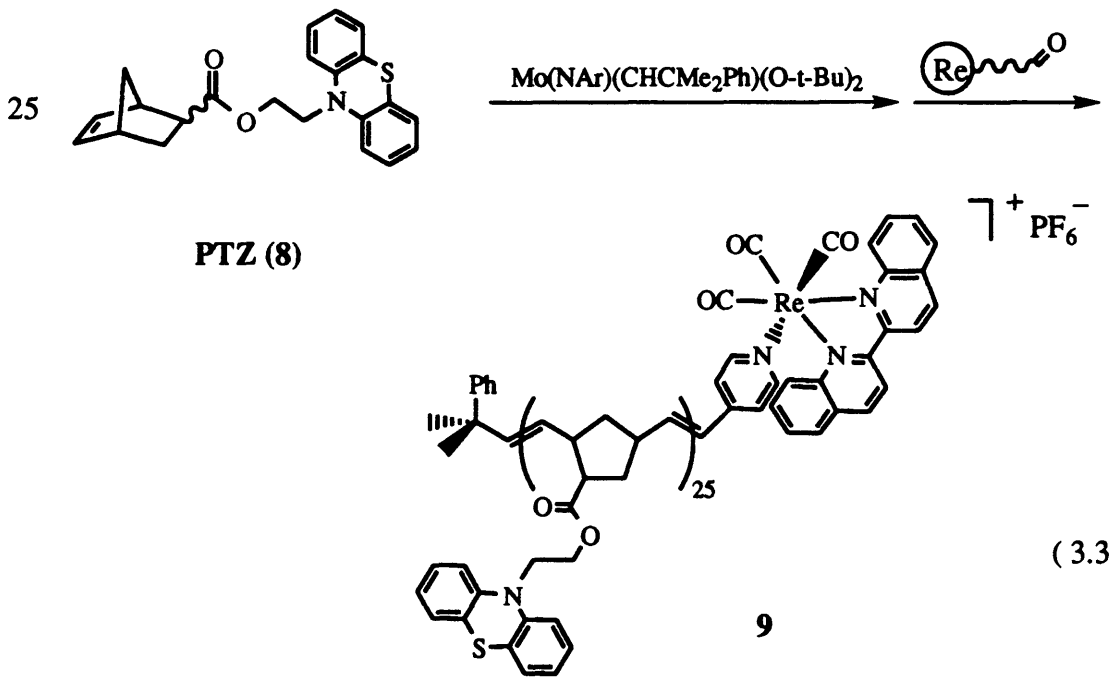


Figure 3.4. Steady-state emission spectra of **6** and $\mathbf{7_{25}}$ and emission decay curve of $\mathbf{7_{25}}$.

$Re(PTZ)_{25}$ homopolymer and $Re(MTD)_x(PTZ)_y$ diblock copolymers

A new redox-active monomer (PTZ, **8**) containing phenothiazine was prepared by Dr. David Albagli and polymerized with $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ catalyst to give $Re(PTZ)_{25}$ (**9**) after capping with **5** (eq 3.3). Complete intramolecular quenching of



(3.3)

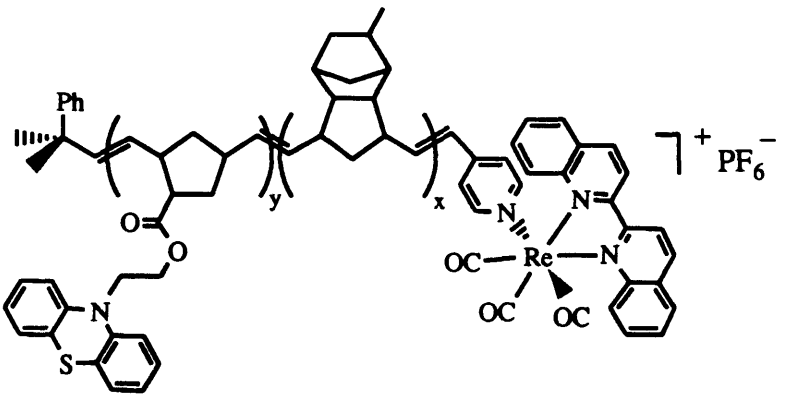
the Re(I) chromophore in **9** was observed by steady-state emission spectroscopy. Photoexcitation of **9** produced an absorption change similar to that found in model compound **3**, and the lifetime of the charge separated state was measured as 38 ns by transient absorption decay kinetics. The longer lifetime is due to either greater distance between the chromophore and donor or delocalization of the hole along the PTZ polymer block. The transient emission and absorption spectroscopy data for **9** and other related polymers described later are summarized in Table 3.1.

A redox-inactive MTD block was interposed between the Re chromophore and PTZ block to make $Re(MTD)_x(PTZ)_y$ polymers ($\mathbf{10_{x,y}}$). Unlike $Re(PTZ)_{25}$, $Re(MTD)_x(PTZ)_y$ ($\mathbf{10_{x,y}}$) did not completely quench the emission of the Re chromophore

Table 3.1. Emission and charge separated state lifetime (ns) in $Re(MTD)_x(PTZ)_y$ block copolymers.

Sample	τ_{em}[a)]	τ_{cs}[a)]
Re(biq) (**5**)	155	--
Re(biq)(PTZ) (**3**)	--	15
$Re(PTZ)_{25}$ (**9**)	--	38
$Re(MTD)_5$ ($\mathbf{7_5}$)	111	--
$Re(MTD)_{25}$ ($\mathbf{7_{25}}$)	137	--
$RE(MTD)_{50}$ ($\mathbf{7_{50}}$)	146	--
$Re(MTD)_{100}$ ($\mathbf{7_{100}}$)	146	--
$Re(MTD)_{200}$ ($\mathbf{7_{200}}$)	163	--
$Re(MTD)_5(PTZ)_{10}$ ($\mathbf{10_{5,10}}$)	33	82
$Re(MTD)_{20}(PTZ)_{10}$ ($\mathbf{10_{20,10}}$)	55	91
$Re(MTD)_{50}(PTZ)_{10}$ ($\mathbf{10_{50,10}}$)	99	93
$Re(MTD)_{100}(PTZ)_{10}$ ($\mathbf{10_{100,10}}$)	105	110
$Re(MTD)_{200}(PTZ)_{10}$ ($\mathbf{10_{200,10}}$)	123	111
$Re(MTD)_{50}(PTZ)_5$ ($\mathbf{10_{50,5}}$)	120	95
$Re(MTD)_{50}(PTZ)_{10}$ ($\mathbf{10_{50,10}}$)	99	93
$Re(MTD)_{50}(PTZ)_{25}$ ($\mathbf{10_{50,25}}$)	98	89
$Re(MTD)_{50}(PTZ)_{50}$ ($\mathbf{10_{50,50}}$)	93	74

(a) τ_{em} of **5** and τ_{cs} of **3** were measured in CH_3CN and τ_{em} and τ_{cs} of all polymers were measured in toluene.

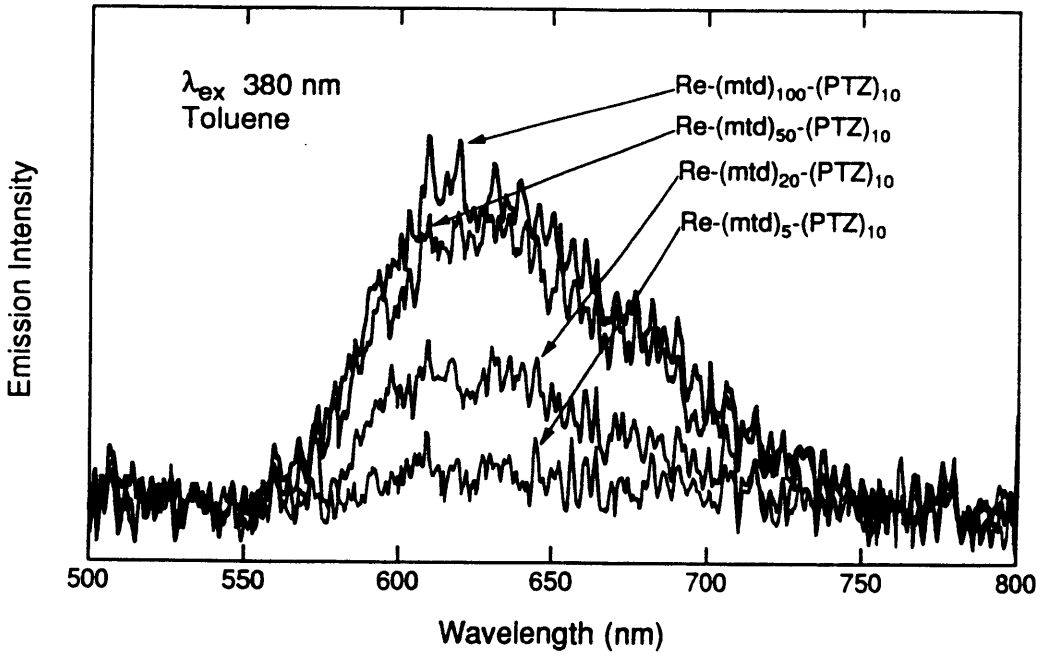


$10_{x,y}$; x = 50, y = 5,10,25,50
x = 5,20,50,100,200, y = 10

and the relative emission quantum yield decreased with the size of the MTD block interposed between the Re(I) center and the PTZ block (Figure 3.5a). The emission lifetimes are in accord with the related emission quantum yield data (Table 3.2). These relative emission quantum yields and emission lifetimes showed saturation behavior when the MTD spacer block length approached 100 units (Figure 3.6). Diblock copolymer series of $Re(MTD)_{50}(PTZ)_y$ showed a shortening of lifetime with the size of the PTZ block (Figure 3.5b). The incomplete quenching suggests that polymer chain dynamics[51-54] govern the quenching efficiency. Further study is required to fully understand the quenching effect, however, the qualitative trends are in accord with expectation.

Transient absorption spectra of $Re(MTD)_x(PTZ)_y$ showed an absorption change similar to that in model complexes **1**, **2** and **3** as shown in Figure 3.7. The absorption decay of the charge separated state at 515 nm was monitored and the lifetime of the charge separated state were measured (see Table 3.1). Selected transient absorption decay curves of charge separated states were shown in Figure 3.8 to demonstrate the effect of the MTD spacer block. Almost a ten-fold increase over the original model complex **3** is observed.

a) $Re(MTD)_x(PTZ)_{10}$



b) $Re(MTD)_{50}(PTZ)_y$

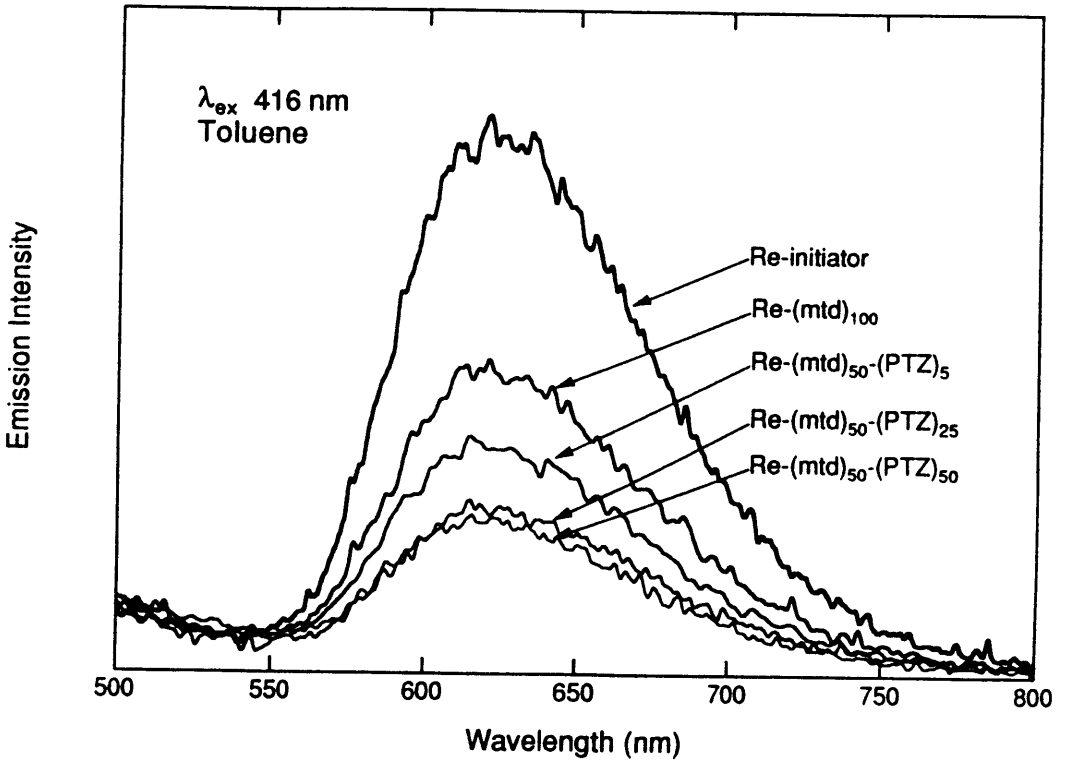


Figure 3.5. Steady-state emission spectra of (a) $Re(MTD)_x(PTZ)_{10}$ and (b) $Re(MTD)_{50}(PTZ)_y$.

Table 3.2. Relative emission quantum yields (Φ_{em}) and emission lifetimes (τ_{em}) of $Re(MTD)_x(PTZ)_y$ block copolymers.

Sample	Φ_{em}	τ_{em}(ns)
$Re(MTD)_{25}$ ($\mathbf{7_{25}}$)	1.00	146
$Re(MTD)_{100}(PTZ)_{10}$ ($\mathbf{10_{100,10}}$)	0.91	105
$Re(MTD)_{50}(PTZ)_{10}$ ($\mathbf{10_{50,10}}$)	0.80	99
$Re(MTD)_{20}(PTZ)_{10}$ ($\mathbf{10_{20,10}}$)	0.38	55
$Re(MTD)_5(PTZ)_{10}$ ($\mathbf{10_{5,10}}$)	0.13	33

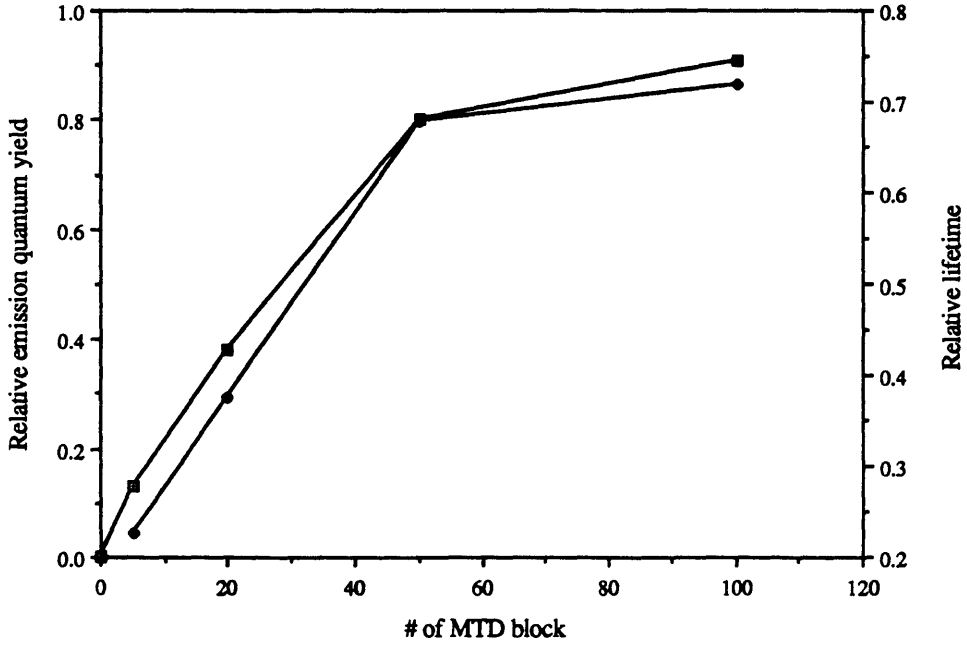


Figure 3.6. Relative emission quantum yields and emission lifetimes of Re chromophore in $Re(MTD)_x(PTZ)_y$.

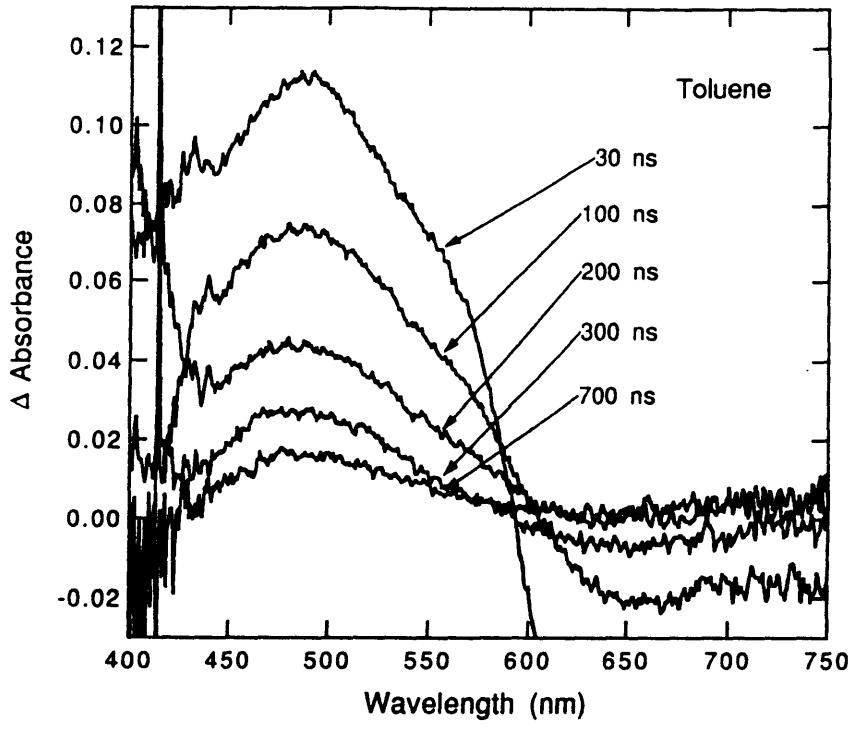


Figure 3.7. Transient absorption of the charge separated state in $Re(MTD)_{50}(PTZ)_{10}$.

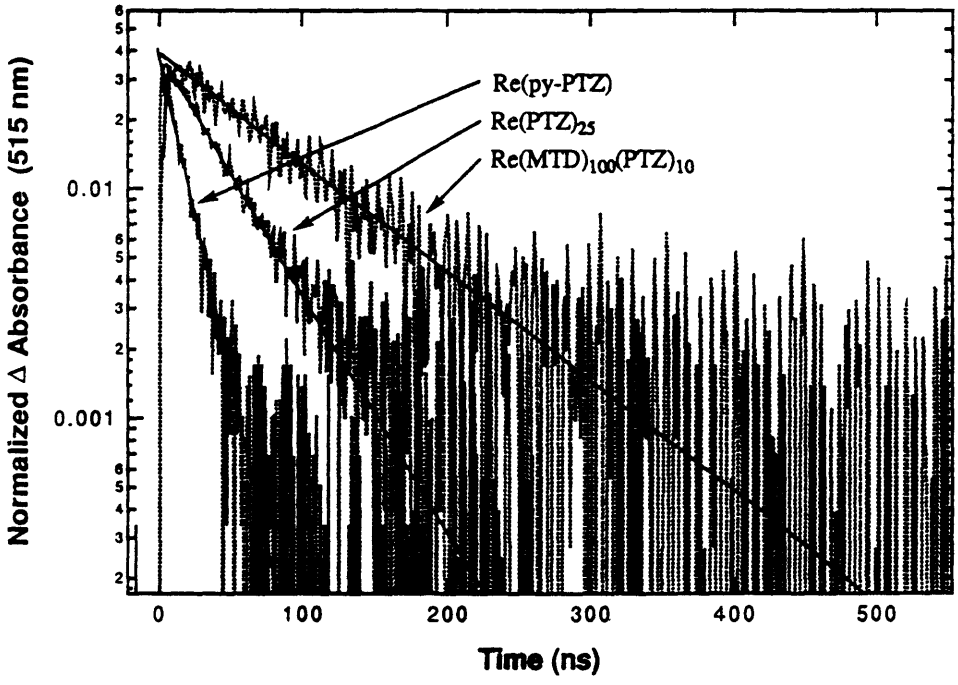
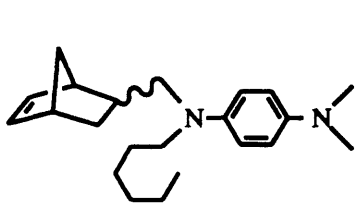


Figure 3.8. Transient absorption decay curves of charge separated states in Re(py-PTZ) (**3**), $Re(PTZ)_{25}$ (**9**) and $Re(MTD)_{100}(PTZ)_{10}$ ($\mathbf{10_{100,10}}$).

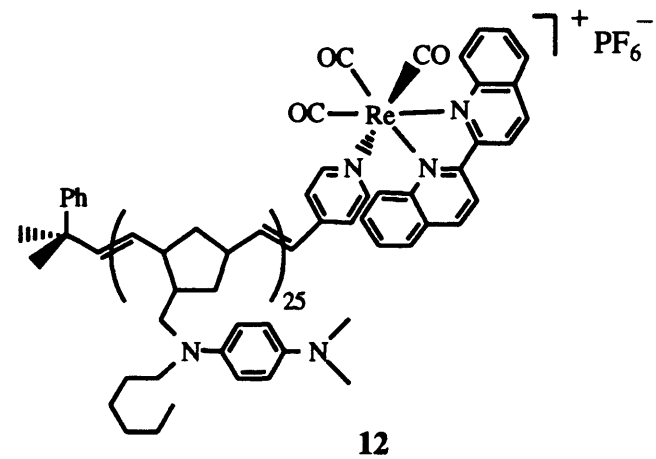
As predicted by the results of forward electron transfer quenching measured by emission lifetime, polymer chain dynamics play a role also in the back electron transfer (measured by charge separated state lifetime). The charge separated state lifetimes of the diblock copolymers, $Re(MTD)_x(PTZ)_y$, increase with the MTD spacer block size and show saturation behavior when the MTD block size approaches 100 units. These results suggest that the presence of the MTD spacer block obviously affects the forward and back electron transfer rates between the Re(I) chromophore and the PTZ donor.

$Re(TMPD)_{25}$ homopolymer and $Re(MTD)_x(TMPD)_y$ diblock copolymers

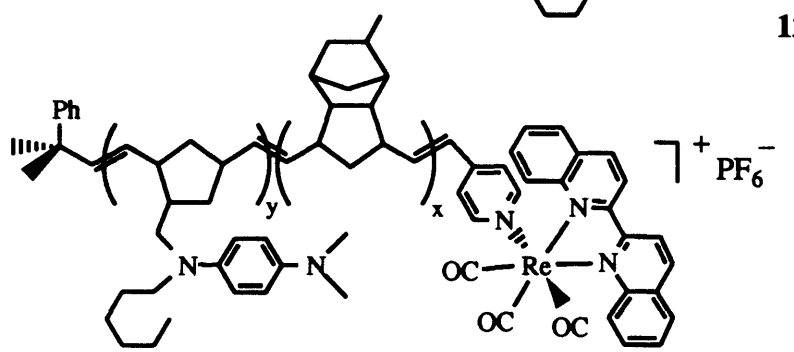
A new monomer (TMPD, **11**) containing the tetramethylphenylenediamine functional group was prepared by Dr. David Albagli. Homopolymer, $Re(TMPD)_{25}$ (**12**), and diblock copolymers, $Re(MTD)_x(TMPD)_y$ (**13**), were prepared by ROMP using



TMPD (11)



12



$13_{x,y}$; x = 25, y = 5
x = 110, y = 10

$Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$. Unlike $Re(TMPD)_{25}$ (**12**) in which the emission was completely quenched, diblock copolymers (**13**) did not completely quench the emission of the Re chromophore and the resulting emission lifetimes could be measured. These emission lifetimes and lifetimes of the charge separated state described later are all summarized in Table 3.3.

Table 3.3. Emission and charge separated state lifetimes (ns) in $Re(MTD)_x(TMPD)_y$ block copolymers.

Sample	τ_{em}(ns)	τ_{cs}(ns)
Re(biq) (**5**)	155	--
Re(biq)(py-TMPD) (**4**)	--	≈ 6
$Re(MTD)_{100}$ (**7_{100}**)	146	--
$Re(TMPD)_{25}$ (**12**)	--	39
$Re(MTD)_{25}(TMPD)_5$ (**$13_{25,5}$**)	92	91
$Re(MTD)_{110}(TMPD)_{10}$ (**$13_{110,10}$**)	111	105

Photoexcitation of **12** and **13** produced an absorption change identical to that in the model complex **4** and the absorption decay of the charge separated state at 568 nm was monitored to measure lifetime (Figure 3.9 and 3.10). The lifetime of the charge separated state of $Re(MTD)_x(TMPD)_y$ were found to be over 15 times longer than that of the model complex **4** (see Table 3.3). As expected in the $Re(MTD)_x(PTZ)_y$ polymers, the presence of the redox-inactive MTD spacer block affects the forward and back electron transfer rates between the Re(I) chromophore and the TMPD donor. Interestingly, the lifetime of the charge separated state of $Re(MTD)_{110}(TMPD)_{10}$ is very close to that of $Re(MTD)_{100}(PTZ)_{10}$. This again indicates that the intramolecular back electron transfer rates are limited by the polymer chain dynamics instead of the electron transfer energetics, since the PTZ has a more favorable back electron transfer reaction, by ~ 0.7 eV .

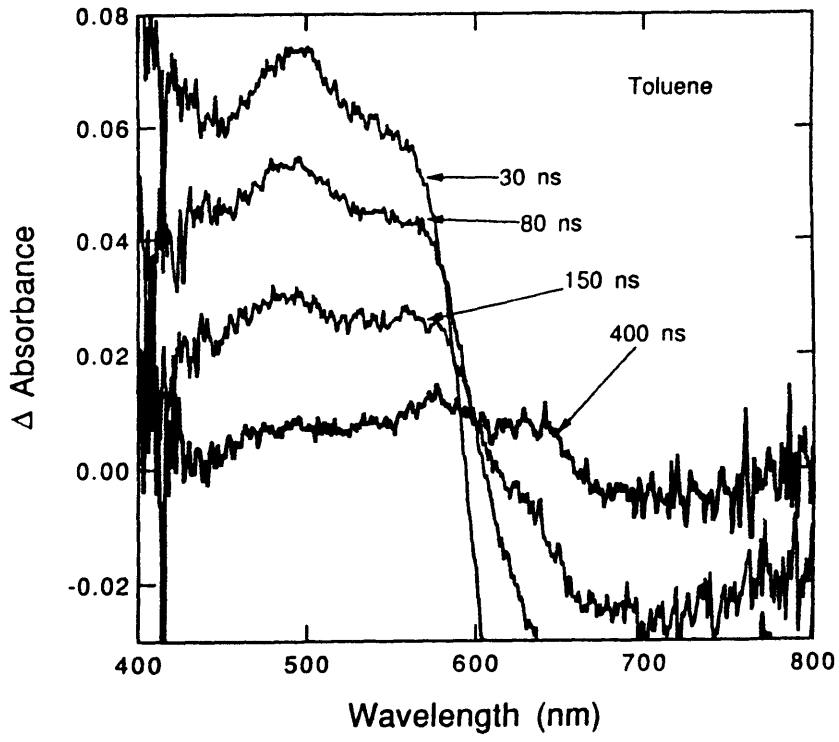


Figure 3.9. Transient absorption of the charge separated state in $Re(MTD)_{25}(TMPD)_5$.

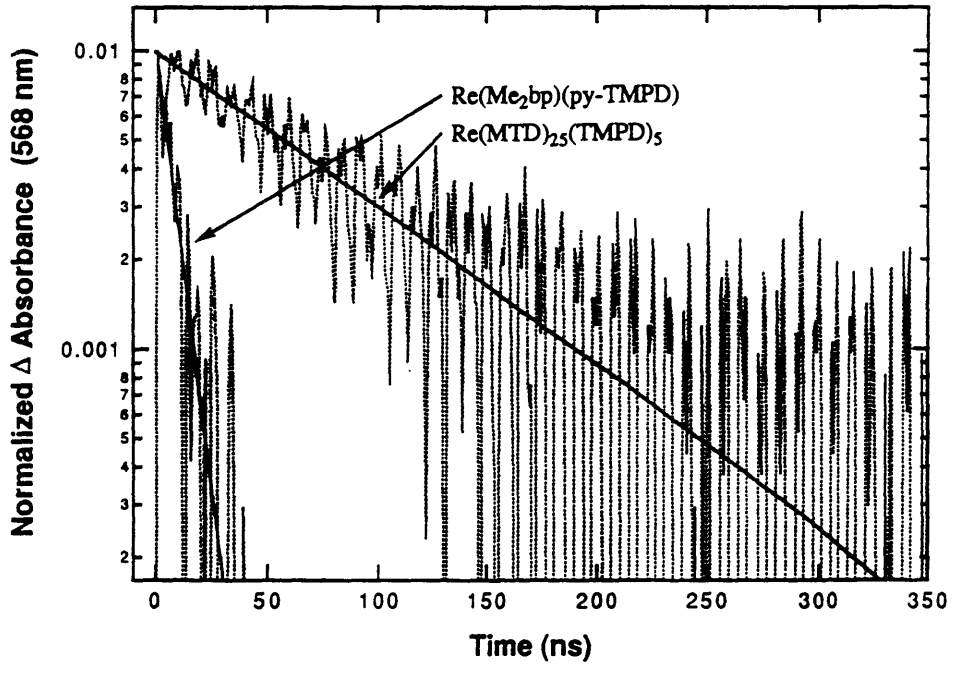
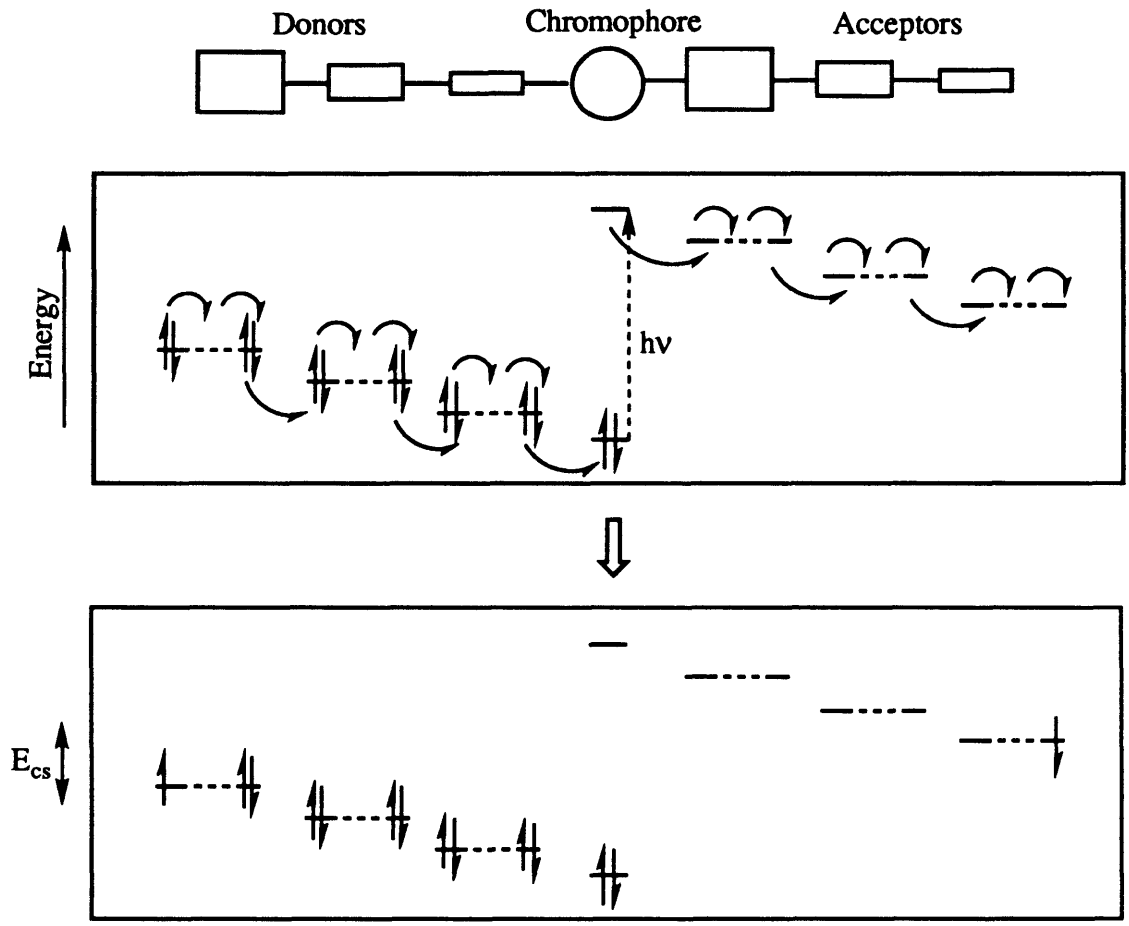


Figure 3.10. Transient absorption decay curves of charge separated states in Re(py-TMPD) (**4**) and $Re(MTD)_{25}(TMPD)_5$ ($\mathbf{13}_{25,5}$).

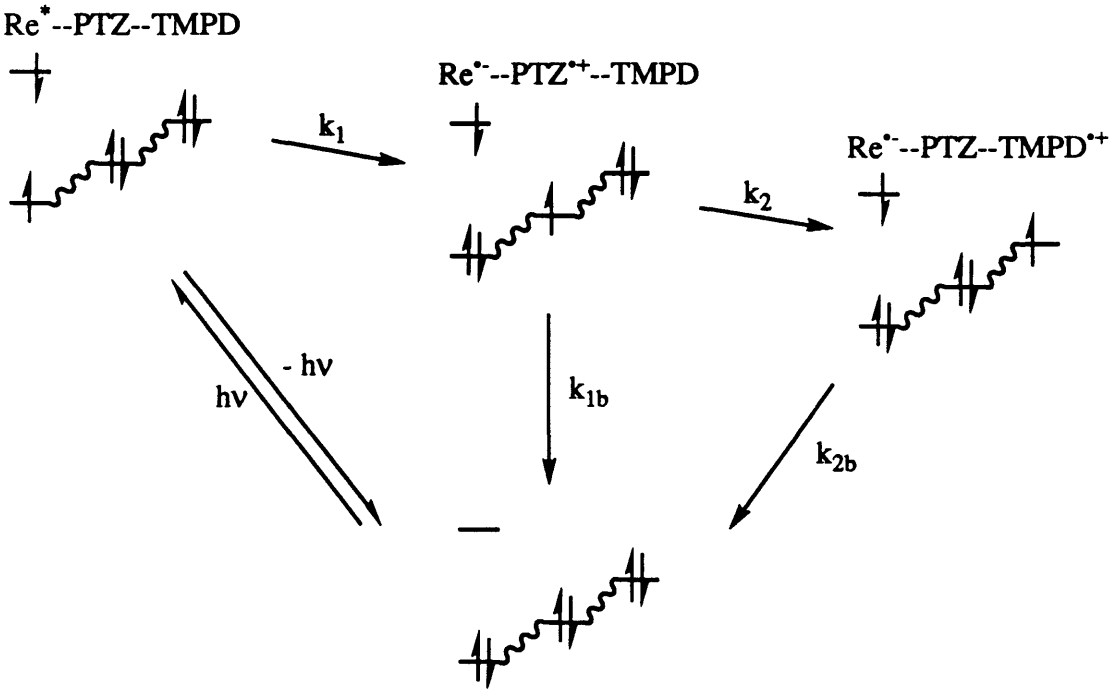
Chain electron transfer

One objective in preparing artificial photosynthesis is to effect unidirectional electron transfer within a molecular system following photoexcitation. The unidirectional transport can be achieved by arranging a sequence of downhill electron transfer (chain electron transfer) by ordering a set of redox reagents according to formal potential. Furthermore, long-lived charge separation might be achieved by providing a sequence of isoenegetic electron transfer to or from a photoexcited center. Chain electron transfer in a multifunctional polymer system is shown in Scheme 3.3.



Scheme 3.3. Photoinduced chain electron transfer in multiblock copolymer with a sequential arrangement of donors and acceptors.

Incorporation of two different electron donors into the polymer should, in principle, allow the second donor group to electron transfer to the first (Scheme 3.4). This step should separate the hole and electron to a greater distance and allow for a



Scheme 3.4. Photoinduced chain electron transfer in a copolymer with two blocks of different donor groups.

longer lived charge separated state. In Scheme 3.4, k_2 must be faster than k_{1b} (and k_{2b}) for the TMPD$^{\bullet+}$ to be observed. With $Re(PTZ)_{25}$, k_1 is very fast ($\approx 10^9$ s^{-1}) and k_{1b} is 2.63×10^7 s^{-1}. For $Re(MTD)_5(PTZ)_{10}$, which has the shortest MTD blocks, k_{1b} is more than two times slower, 1.22×10^7 s^{-1}. This is the rate with which intramolecular chain electron transfer must be completed. Diffusion controlled chain electron transfer in solution as a model system was carried out with **5**, methylphenothiazine (Meptz) and tetramethylphenylenediamine (tmpd) (Figure 3.11). Excitation of **5** with 10^{-2} M Meptz

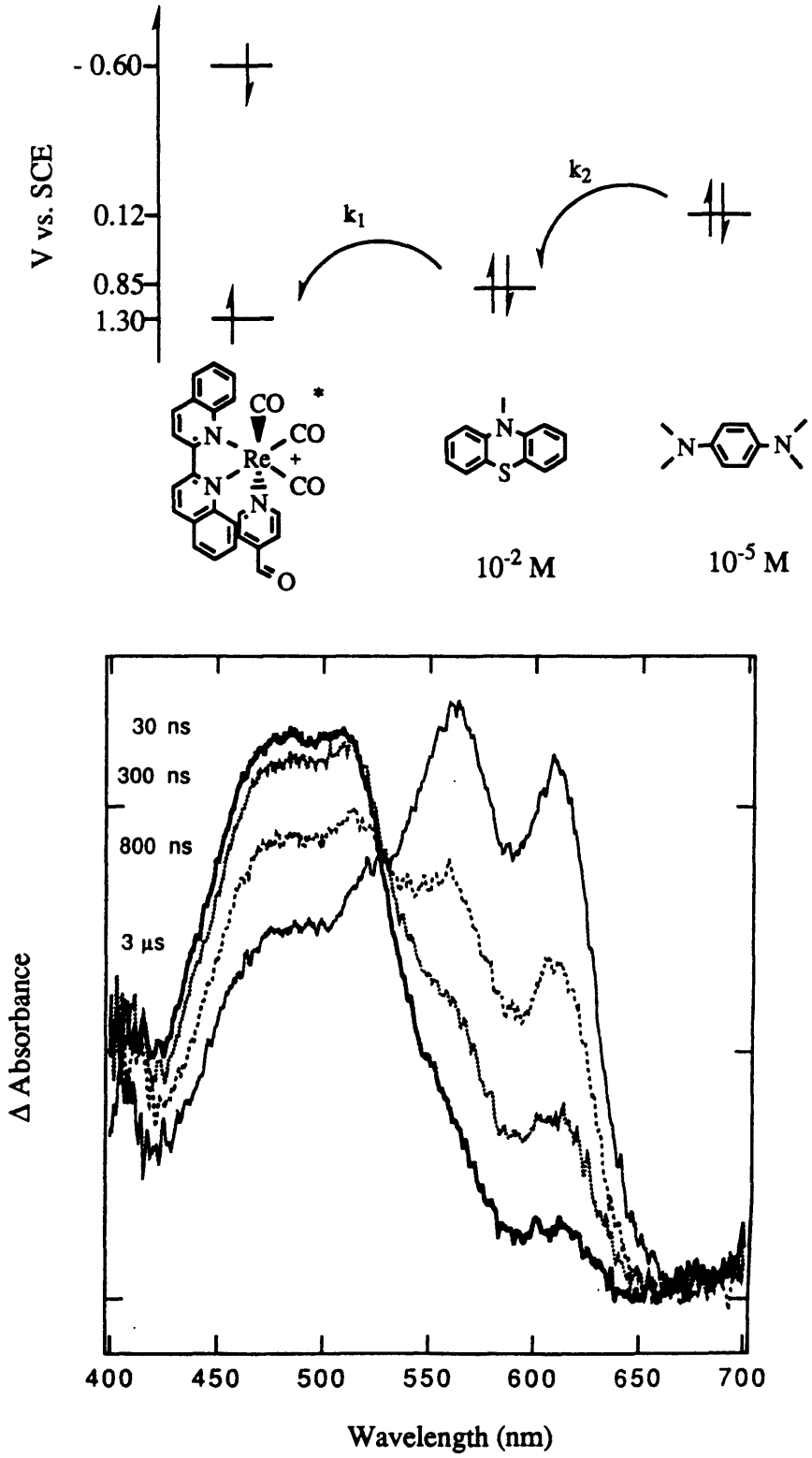


Figure 3.11. Energetics for chain electron transfer and spectra produced at the indicated times following the quenching of Re(biq)(py-CHO) (**5**) by 10^{-2} M Meptz and 10^{-5} M tmpd CH_3CN / 0.1 M $[(n\text{-}Bu)_4N]PF_6$.

and 10^{-5} M tmpd in CH_3CN with 0.1 M $[(n\text{-}Bu)_4N]PF_6$ produced $Meptz^{\bullet+}$ and Re(py-CHO)($biq^{\bullet-}$) within the first 30 ns. From 30 ns to 3 μs absorption due to $tmpd^{\bullet+}$ grew in as $Meptz^{\bullet+}$ was quenched by the encountered tmpd in solution.

$Re(PTZ)_{25}(TMPD)_5$ diblock copolymer and $Re(MTD)_x(PTZ)_y(TMPD)_z$ triblock copolymers

$Re(PTZ)_{25}(TMPD)_5$ was prepared using $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ as a catalyst. Photoexcited emission and absorption spectroscopy of these polymers showed a complete quenching of emission. No absorption from $TMPD^{\bullet+}$ was detected due to the fast back electron transfer from the reduced Re center to the oxidized donor $PTZ^{\bullet+}$. Another series of triblock copolymers which have MTD spacer blocks between the Re chromophore and PTZ block, $Re(MTD)_x(PTZ)_y(TMPD)_z$, were prepared in an analogous way. Following photoexcitation, all three polymers showed partial quenching of the Re emission and transient absorption consistent with a combination of $PTZ^{\bullet+}$ and $TMPD^{\bullet+}$. The emission lifetimes and charge separated state lifetimes in toluene are summarized along with those of the model polymers in Table 3.4. The absorption decays of triblock copolymers were monitored at 515 nm, where $PTZ^{\bullet+}$ strongly absorbs while $TMPD^{\bullet+}$ does not absorb, and at 568 nm where $TMPD^{\bullet+}$ strongly absorbs and $PTZ^{\bullet+}$ does not. The transient absorption spectra of the charge separated state for $Re(MTD)_{100}(PTZ)_{10}(TMPD)_{10}$ at different times following photoexcitation are shown in Figure 3.12. Based on the absorption decay data at 568 nm, there is no evidence for chain electron transfer as detected in termolecular chain electron systems (Figure 3.11). PTZ and TMPD donors seem to compete the electron transfer to the excited Re chromophore and lifetimes of the charge separated state are very similar in both donors. These results again indicate that the polymer chain dynamics, rather than the energetics, limit the forward and back electron transfer.

Table 3.4. Emission lifetimes (τ_{em}) and charge separated state lifetimes (τ_{cs}) of $Re(MTD)_x(PTZ)_y(TMPD)_z$.

Sample	τ_{em}(ns)	τ_{cs}(ns) 515 nm	τ_{cs}(ns) 568 nm
$Re(PTZ)_{25}$ (**9**)	--	38	--
$Re(TMPD)_{25}$ (**12**)	--	--	39
$Re(PTZ)_{25}(TMPD)_5$	--	36	--
$Re(MTD)_{100}$ ($\mathbf{7_{100}}$)	146	--	--
$Re(MTD)_{100}(PTZ)_{10}$ ($\mathbf{10_{100,10}}$)	105	110	--
$Re(MTD)_{110}(TMPD)_{10}$ ($\mathbf{13_{110,10}}$)	111	--	105
$Re(MTD)_{100}(PTZ)_{10}(TMPD)_{10}$	101	85	88
$Re(MTD)_{100}(PTZ)_{50}(TMPD)_{10}$	96	83	87
$Re(MTD)_{200}(PTZ)_{10}$ ($\mathbf{10_{200,10}}$)	123	111	--
$Re(MTD)_{200}(PTZ)_{10}(TMPD)_{10}$	116	103	103

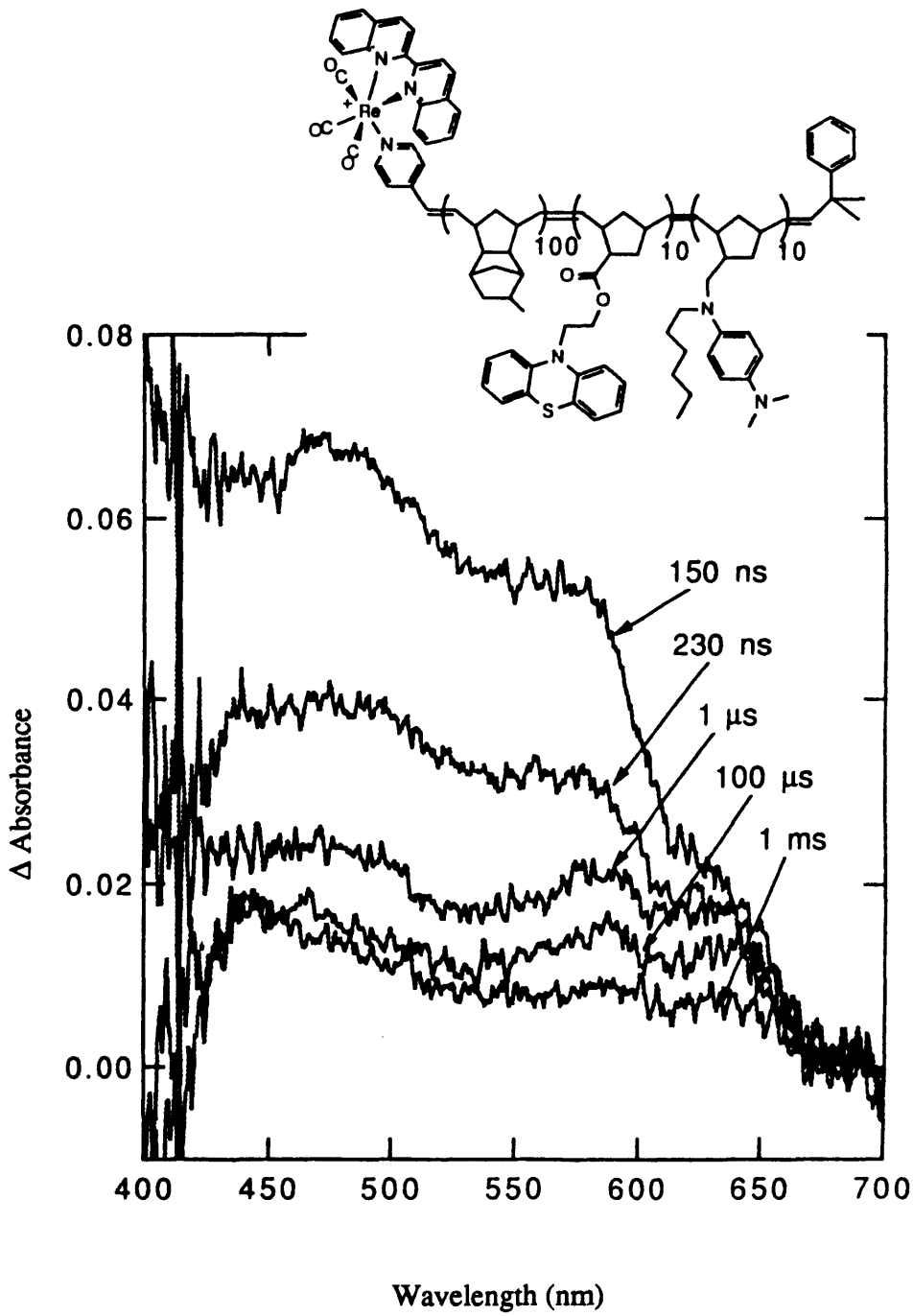


Figure 3.12. Transient absorption of triblock copolymer $Re(MTD)_{100}$-$(PTZ)_{10}(TMPD)_{10}$.

CONCLUSIONS

Novel Re(I) chromophore-capped polymers of monomer containing donor molecules such as phenothiazine or tetramethylphenylenediamine were prepared by ROMP using $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ as a catalyst. These Re(I) chromophore-capped polymers showed well-behaved photoinduced intramolecular electron transfer, which was detected by transient absorption and transient emission spectroscopy. Lifetimes of the charge separated state were measured by transient absorption decay kinetics. For example, when the redox-inactive MTD block was interposed as a spacer block between the Re(I) chromophore and donor blocks in order to suppress the back electron transfer rate, lifetimes (τ_{cs}) of the charge separated state were increased two orders of magnitude compared to that of model complexes (**3** and **4**). However, the intramolecular forward and back electron transfer rates seem to be limited by polymer chain dynamics rather than electron transfer energetics because, even though they are more rigid than polystyrene or polymethyl methacrylate,[43] ROMP polymers are flexible in solution.

In this chapter new photoactive polymer systems capable of separating charges upon photoexcitation were introduced. These polymers have shown great potential in fundamental electron transfer and polymer chain dynamics, and as molecular units for photoenergy conversion or molecular electronic devices. Chain electron transfer in multiblock copolymer has not been observed, however, which might duplicate the photosynthetic z-scheme of unidirectional electron transfer[55] probably due to the flexibility of ROMP polymers in solution which permits direct interaction of chromophore and donor molecules in a multiblock system. A more rigid polymer system and phase separation of each blocks are needed to solve the flexible polymer backbone problem and future work on such systems should prove fruitful.

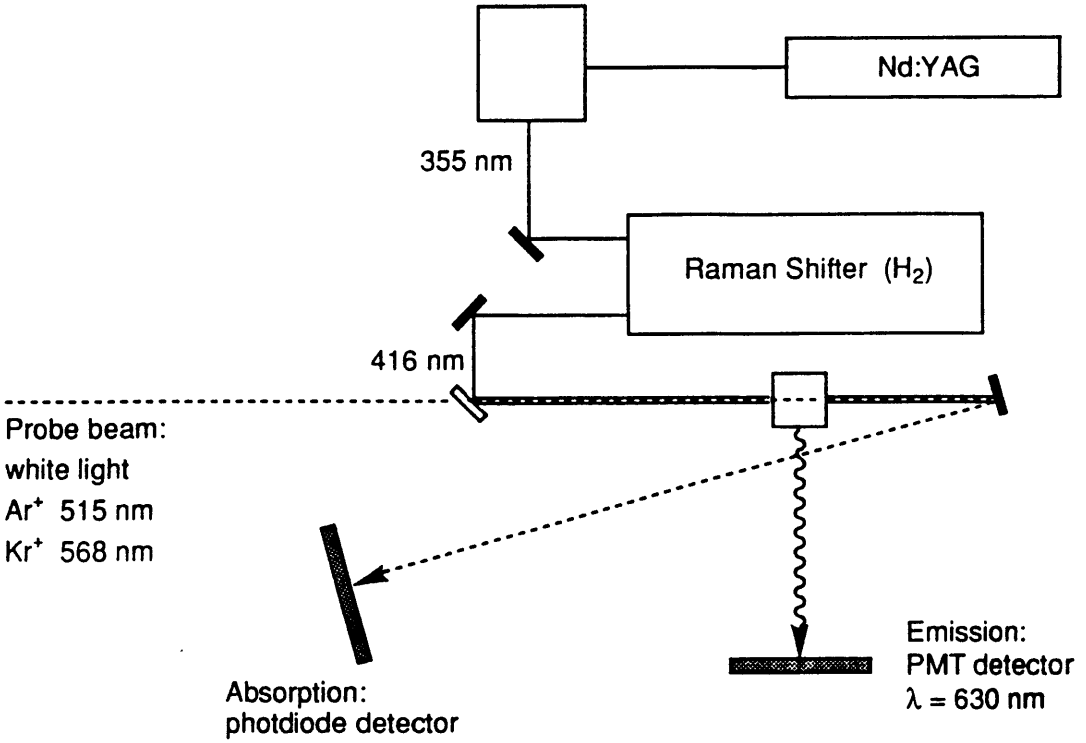
EXPERIMENTAL PROCEDURES

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade THF was vacuum transferred twice from sodium benzophenone ketyl. Polymerization grade toluene was stored over sodium / potassium alloy and passed through alumina prior to use.

HPLC grade solvents were used in Gel permeation chromatography (GPC) runs and were degassed prior to use. GPC was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Viscotek Differential Refractometer / Viscometer H-500, and a Spectroflow 757 absorbance detector on a samples 0.1 - 0.3% (w/v) in THF which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 - 2.75 x 10^6. NMR data were obtained at 300 MHz and listed in parts per million downfield from tetramethylsilane. Spectra were obtained at 25°C unless otherwise noted. Transient emission and transient absorption laser systems are described elsewhere[49,50] and the schematic diagram is shown in Scheme 3.5.

$Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ was prepared as described in the literature.[56] Methyltetracyclododecene (MTD) was generously supplied from Goodrich and purified by the distillation over Na. Re(biq)(py-PTZ) (**3**), $Re(Me_2\text{-}bp)$(py-TMPD) (**4**), monomers of PTZ (**8**) and TMPD (**11**) were prepared by Dr. David Albagli[57] and capping reagent Re(biq)(py-CHO) (**5**) was prepared by Dr. Eric J. Lee.[49]

Reaction of $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ with Re(biq)(py-CHO) (5). $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ (10.0 mg, 18.2 μmol) was dissolved in 1 mL of CD_2Cl_2 and Re(biq)(py-CHO) (**5**, 14 mg, 18.2 μmol) was added. After the mixture was shaken



Scheme 3.5. Diagram of the apparatus for transient and time-resolved spectroscopic measurements.

for 10 min, the mixture was transferred into a NMR tube and checked by NMR to see the completion of the reaction. This solution was passed through a silica gel in order to remove the metal-oxo complex. The product was eluted as a orange band with a THF eluent. Absorption and emission spectra of coupled product showed identical peaks as **5**: ^{1}H NMR (CD_2Cl_2) δ 8.93 (d, 2, biq H_{aryl}), 8.80 (d, 2, biq H_{aryl}), 8.42-7.92 (m, 8, biq H_{aryl}), 7.22 (m, 5, Ph H_{aryl}), 7.09 (d, 2, py H_o), 6.90 (d, 2, py H_m), 6.60 and 6.18 (d, 1, alkene), 1.40 (s, 6, CH_3).

Polymerization. All the polymerization were carried out under N_2 in Vacuum Atmospheres drybox. THF was used as a solvent for the polymerizations. Each monomer was polymerized for 30 min and the polymerization was terminated by adding 2.5 equiv of Re(biq)(py-CHO) (**5**). The mixture was stirred for 15h and the polymer was precipitated from methanol. Polymerization yields were normally higher than 93%, except for several short polymers because of problems with precipitation from methanol. A typical experimental procedure for the synthesis of $Re(MTD)_{100}(PTZ)_{10}$ is described below. $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ (5.0 mg, 9.1 μmol) was dissolved in 1 mL of THF. PTZ (**8**, 3 mg, 91 μmol) was dissolved in 0.5 mL of THF and added at once to a stirred solution of catalyst. After 30 min, MTD (159 mg, 910 μmol) solution in 1 mL of THF was added to a living polymer solution and the mixture was stirred for another 30 min. Re(biq)(py-CHO) (**5**, 18 mg, 22.8 μmol) was added and the mixture was stirred for 15h. Polymer (192 mg, 99%) was isolated by the precipitation from methanol followed vacuum drying. The attempt to characterize the polymers by GPC failed probably due to the ionic sites of the polymer interacting with the stationary phase of the column. NMR spectra of the polymers, however, showed a new broad alkene resonance at 5.30 ppm. No residual monomer resonances were detected. Benzaldehyde-capped polymers were prepared in order to check the molecular weight distribution of polymers. Homopolymer of PTZ, $Ph(PTZ)_{25}$, showed a unimodal GPC trace with M_n = 10,600 and M_w / M_n = 1.14, while the triblock copolymer, $Ph(MTD)_{100}(PTZ)_{10}(TMPD)_{10}$, showed a unimodal GPC trace with M_n = 69,900 and M_w / M_n = 1.62.

REFERENCES

(1) Roth, H. D. *Top. Curr. Chem.* **1990**, *156*, 1.

(2) Eland, J. H. D. "Photoelectron Spectroscopy"; Wiley: New York, 1984.

(3) Albini, A. *Synthesis* **1981**, 249.

(4) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(5) Connolly, J. S. "Photochemical conversion and storage of solar energy"; Academic: New York, 1981.

(6) Wrighton, M. S. in "Fine Chemicals for the Electronics Industry"; P. Bamfield, Ed.; The Royal Society of Chemistry: London, 1986; Vol. 60; pp 53.

(7) Gust, A.; Moore, T. A. in "Supramolecular photochemistry"; V. Balzani, Ed.; Riedel: Dordrecht, 1987; pp 267.

(8) Chanon, M.; Fox, M. A. "Photoinduced Electron Transfer"; Elsevier: Amsterdam, 1988.

(9) Fox, M. A. *Top. Curr. Chem.* **1991**, *159*, 67.

(10) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.

(11) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562.

(12) Gust, D.; Moore, T. A. *Science* **1989**, *244*, 35.

(13) Gust, D.; Moore, T. A. *Top. Curr. Chem.* **1991**, *159*, 103.

(14) Gust, D.; Moore, T. A.; Moore, A. L.; Macpherson, A. N.; Lopez, A.; Degraziano, J. M.; Gouni, I.; Bittersmann, E.; Seely, G. R.; Gao, F.; Nieman, R. A.; Ma, X. C. C.; Demanche, L. J.; Hung, S. C.; Luttrull, D. K.; Lee, S. J.; Kerrigan, P. K. *J. Am. Chem. Soc.* **1993**, *115*, 11141.

(15) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163.

(16) Meyer, T. J. *Prog. Inorg. Chem.* **1983**, *30*, 389.

(17) Chen, P.; Westmoreland, T. D.; Danielson, E.; Schanze, K.; Anthon, D.; Neveux, P. E.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116.

(18) Chen, P.; Duesing, R.; Tapolsky, G.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8305.

(19) Westmoreland, T. D.; Schanze, K. S.; Neveux, P. E., Jr.; Danielson, E.; Sullivan, B. P.; Chen, P.; Meyer, T. J. *Inorg. Chem.* **1984**, *24*, 2596.

(20) Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 2519.

(21) Christ, C., Jr.; Yu, J.; Zhao, X.; Palmore, G. T. R.; Wrighton, M. S. *Inorg. Chem.* **1992**, *31*, 4439.

(22) Schoonover, J. R.; Strouse, G. F.; Chen, P.; Bates, W. D.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 2618.

(23) Gil, C.; Christ, C., Jr.; Wrighton, M. S. "unpublished results,"

(24) Guillet, J. "Polymer Photophysics and Photochemistry"; Cambridge University Press: Cambridge, UK, 1985.

(25) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571.

(26) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.

(27) White, B.; Nowakowska, M.; Vancso, G. J.; Guillet, J. E. *Macromolecules* **1991**, *24*, 2903.

(28) Itoh, Y.; Nakada, M.; Satoh, H.; Hachimori, A.; Webber, S. E. *Macromolecules* **1993**, *26*, 1941.

(29) Baxter, S. M.; Jones, W. E., Jr.; Danielson, E.; Worl, L.; Strouse, G.; Younathan, J.; Meyer, T. J. *Coord. Chem. Rev.* **1991**, *111*, 47.

(30) Jones, W. E.; Baxter, S. M.; Strouse, G. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1993**, *115*, 7363.

(31) Bai, F.; Chang, C.-H.; Webber, S. E. *Macromolecules* **1993**, *26*, 1941.

(32) Xu, R. L.; Winnik, M. A. *J. Photochem. Photophys., A* **1991**, *57*, 351.

(33) Winnik, M. A.; Xu, H.; Marthinho, J. M. G. *Polymer* **1991**, *32*, 84.

(34) Duhamel, J.; Winnik, M. A.; Baros, F.; Andre, J. C.; Martinho, J. M. G. *J. Phys. Chem.* **1992**, *96*, 9805.

(35) Liu, G. *Macromilecules* **1992**, *25*, 5805.

(36) Maptinho, J. M. G.; Sousa, A. T. R.; Winnik, M. A. *Macromolecules* **1993**, *26*, 4484.

(37) Fox, M. A.; Jones, W. E., Jr.; Watkins, D. M. in "Chem. and Eng. News"; 1993; pp 38.

(38) Fox, M. A. *Acc. Chem. Res.* **1992**, *25*, 569.

(39) Fox, M. A.; Britt, P. F. *Macromolecules* **1990**, *23*, 4533.

(40) Allen, G.; Bevington, J. C. "Comprehensive Polymer Science"; Pergamon Press: Oxford, 1989; Vol. 3 and 4.

(41) Albagli, D.; Bazan, G. C.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150.

(42) Albagli, D.; Bazan, G.; Schrock, R. R.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97*, 10211.

(43) Watkins, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6441.

(44) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(45) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 24.

(46) Albagli, D.; Bazan, G. C.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 7328.

(47) Hickman, J. J.; Ofer, D.; Zou, C.; Wrighton, M. S.; Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 1128.

(48) Finklea, H. O.; Hanshew, D. D. *J. Am. Chem. Soc.* **1992**, *114*, 3173.

(49) Lee, E. J. Ph.D. Thesis, M.I.T., 1993.

(50) Zhao, X. Ph. D. Thesis, M.I.T., 1994.

(51) Wilemski, G.; Fixman, M. *J. Chem. Phys.* **1974**, *60*, 866.

(52) O'Shaughnessy, B. *J. Chem. Phys.* **1990**, *94*, 4042.

(53) Liu, G. *Macromolecules* **1993**, *26*, 6998.

(54) Friedman, B.; O'Shaughnessy, B. *Macrimolecules* **1993**, *26*, 5726.

(55) Livorness, J.; Smith, T. D. *Struc. and Bond.* **1982**, *48*, 1.

(56) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(57) Albagli, D.; Lee, E. J.; Zhao, X.; Wrighton, M. S.; Lee, J.-K.; Schrock, R. R. "unpublished results,"

CHAPTER 4

The Synthesis of Polymers Containing Both Unsaturated Conjugated Chains and Metal Nanoclusters

INTRODUCTION

There has been a significant amount of research on the nonlinear optical (NLO) behavior of organic molecules and polymers having conjugated π-systems.[1-4] They have been studied extensively because they have several advantages over inorganic materials, e.g., relatively large optical nonlinearity and very fast response time. Furthermore, organic NLO materials are relatively inexpensive and easy to process compared to inorganic NLO materials such as single crystals of $LiNbO_3$.[5,6] Polyacetylene has been studied for electrical and optical properties. Despite its highly conductive property, especially when doped[7] and oriented,[8] as well as its high third-order susceptibility ($\chi^{(3)}$),[9,10] polyacetylene is insoluble and very unstable in air. Although favorable properties of polyacetylene has been predicted by many theorists, the insolubility and instability of this class of polymer has hampered its systematic study. Recently soluble triblock copolymers that contain polyene in the center block were prepared by ROMP and the dependence of $\chi^{(3)}$ on conjugation length was measured as 3.6,[11] which agree well with calculated values ranging from 3 to 5.4.[12-18] Substituted polyenes were prepared by a living cyclopolymerization of derivatives of 1,6-heptadiyne using Mo(NAr)-(CHR)$(OR_{F6})_2$ as the initiator in DME.[19,20] A preliminary study of the second hyperpolarizability (γ) for the phenyl capped symmetric cyclopolyenes showed a definite proportionality between γ and conjugation length and also the first experimental evidence for saturation of γ.[21]

It has been known that the third-order susceptibility ($\chi^{(3)}$) of the material can be enhanced by doping with small metal spheres (nanoclusters).[22-25] These nanoclusters enhance the local fields by causing the applied field lines to bend in and concentrate at their surface and increase $\chi^{(3)}$ (which is proportional to the fourth power of the electric field) as large as 10^8 times. For example, poly(methylmethacrylate) (PMMA) was doped with silver nanoclusters (≈ 15 nm) to concentrations of 0.045% by weight and $\chi^{(3)}$ of doped PMMA was measured to be at least 5 orders of magnitude larger than that of

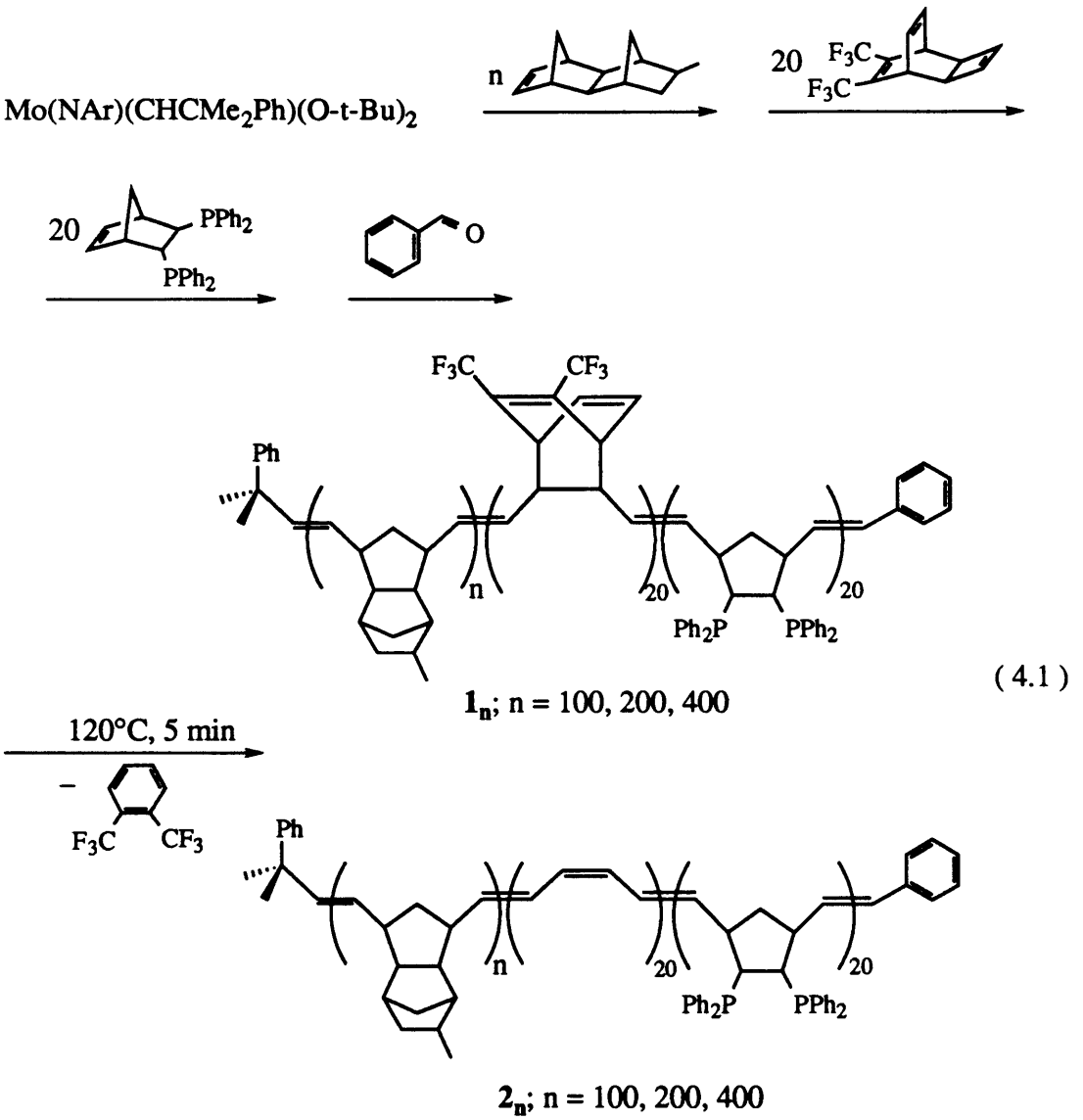
undoped PMMA.[26] Recently a method has been developed in our group to create a nanocluster / polymer composite material by ROMP techniques. In this technique, metal nanoclusters are synthesized within diblock copolymer microdomains. For example, gold and silver clusters were generated from diblock copolymers in which the metal atoms were attached to each repeat unit of one of the bolcks in a ROMP block copolymer via coordination to a phosphine center.[27,28] The block copolymers exhibited microphase separation, and thermal treatment of the polymer films resulted in the formation of silver and gold clusters less than 10 nm in diameter that resided mostly within the original microdomains. Analogous synthesis of metal sulfide semiconductor clusters within diblock copolymer microdomains has also been reported.[29-34]

In this chapter, several synthetic efforts to prepare polymers by ROMP or a living cyclopolymerization are discussed, which contain both unsaturated conjugated block and metal nanoclusters. These polymers are expected to show large NLO properties from the combined effects of π-conjugated electrons and nanoclusters. It has already been proposed that large enhancements in $\chi^{(3)}$ may be achieved by either coating the surface of the metal nanocluster with the conjugated NLO materials or by doping the metal nanocluster within the conjugated materials boundary.[35]

RESULTS AND DISCUSSION

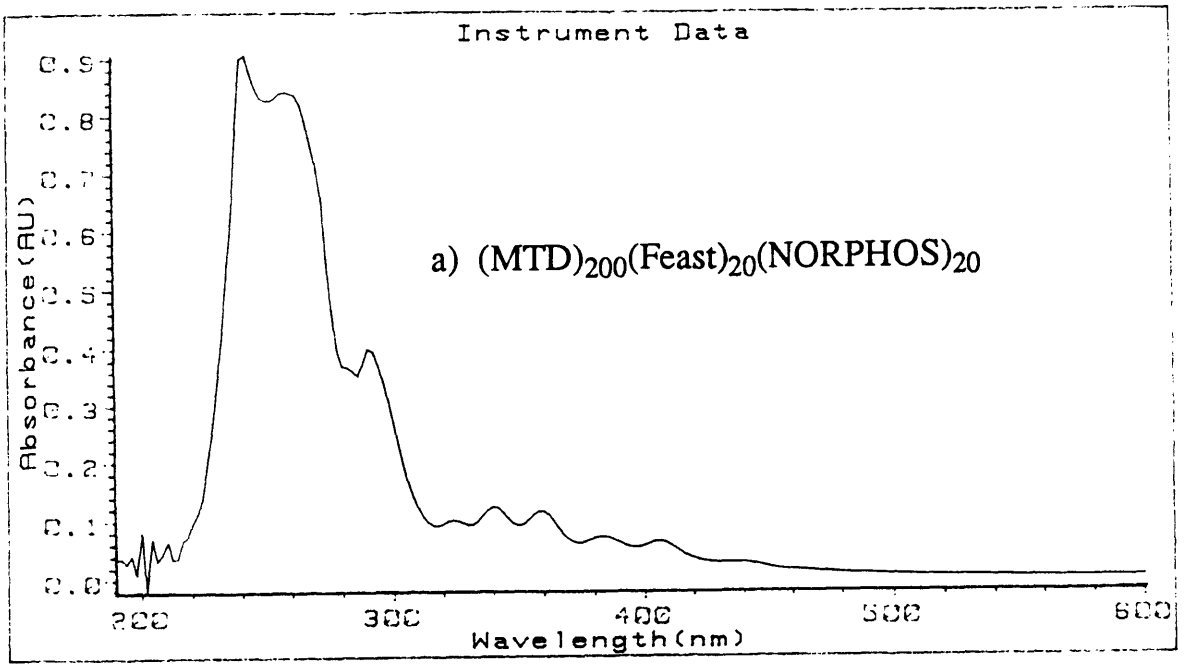
Polyenes with a precursor complex of silver cluster

Three different monomers, methyltetracyclododecene (MTD), 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (Feast) and racemic 2-exo-3-endo-bis(diphenylphosphino)bicyclo[2.2.1]heptene (NORPHOS), were polymerized successively in toluene with Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$ catalyst and capped with benzaldehyde to afford triblock copolymers $\mathbf{1_n}$ in a high yield (eq 4.1). These polymers are yellow in



(4.1)

color and show the finger type of UV absorption between 300-450 nm, which results from the short sections of conjugated double bonds generated by a retro Diels-Alder reaction during the polymerization (Figure 4.1.a).[36,37] After the polymer solutions were heated at 120°C for 5 min, new deep-red colored triblock copolymers $\mathbf{2_n}$ were generated, which contain a polyene block in the middle of polymer chain. These new polymers were very soluble in normal organic solvent such as THF, benzene and toluene. Their



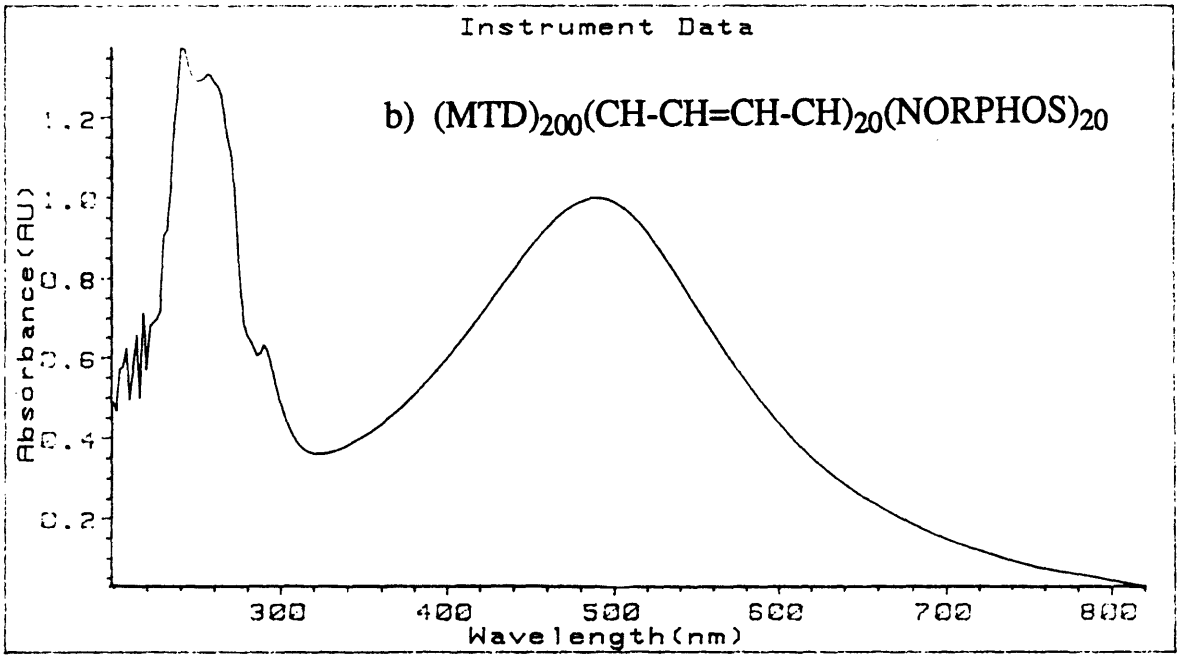
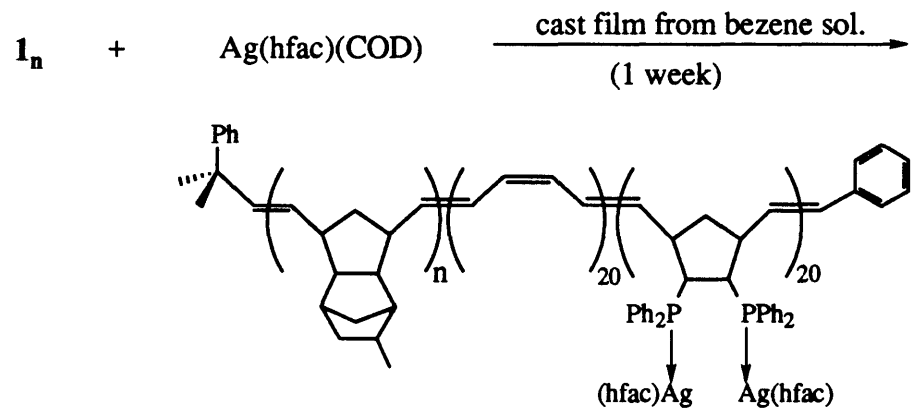


Figure 4.1 UV spectra of (a) $\mathbf{1}_{200}$ and b) $\mathbf{2}_{200}$ in THF.

UV spectra (Figure 4.1.b) showed broad absorption bands with a maximum at 490 nm consistent with the known result of soluble triblock copolymers of $(MTD)_n(CH=CH)_m$-$(MTD)_n$ or $(Norbornene)_n(CH=CH)_m(Norbornene)_n$.[11,38] When solvent was slowly evaporated from a solution of $\mathbf{1_n}$ and Ag(hfac)(COD) (hfac = hexafluoroacetylacetate, COD = cyclooctadiene) in benzene in the presence of a small amount of COD to prevent the decomposition of Ag(hfac)(COD) during the film casting[27,28], deep-red colored polymer ($\mathbf{2_n}$-**Ag(hfac)**) films were prepared; the retro Diels-Alder reaction was completed during the film casting because it took approximately 7 days (eq 4.2).



(4.2)

Transmission electron microscopy (TEM) micrograph of $\mathbf{2_{400}}$-**Ag(hfac)** showed an irregular pattern while those of $\mathbf{2_{200}}$-**Ag(hfac)** and $\mathbf{2_{100}}$-**Ag(hfac)** showed lamella morphology (Figure 4.2.a), one microdomain containing MTD block and the other containing Feast and NORPHOS blocks. All three polymers generated silver clusters ($\mathbf{2_n}$-**Ag**) after the microtomed polymer films on the TEM grid were heated at 150°C for 13h (Table 4.1). The silver clusters resided mostly in the microdomain in which the silver complex was originally located (Figure 4.2.b). Heat treatment of the bulk polymer films of $\mathbf{2_n}$-**Ag(hfac)** gave very brittle polymer films of $\mathbf{2_n}$-**Ag** making microtoming

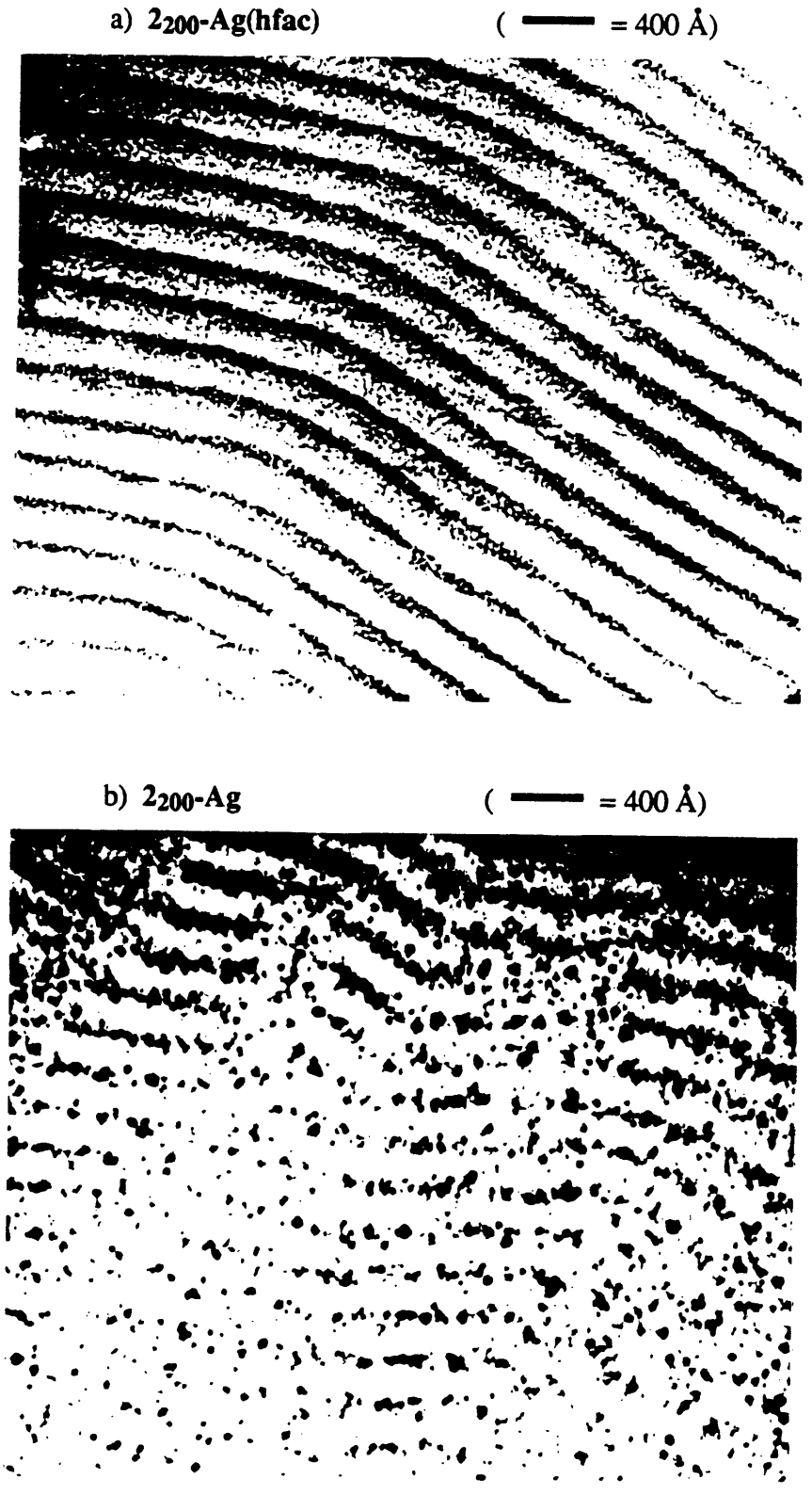


Figure 4.2 TEM micrographs of (a) 2_{200}-Ag(hfac) and (b) 2_{200}-Ag after heat treatment.

Table 4.1 Silver containing triblock copolymers.

	[Ag]%[a]	Ag%[b]	morphology	cluster size[c]
2_{400}	25	4.6	irr. pattern	10 - 30 nm
2_{200}	39	7.4	lamella	5 - 10 nm
2_{100}	57	10.6	lamella	5 - 10 nm

a) percentage of silver containing block. b) percentage of silver atom.
c) after heat treatment.

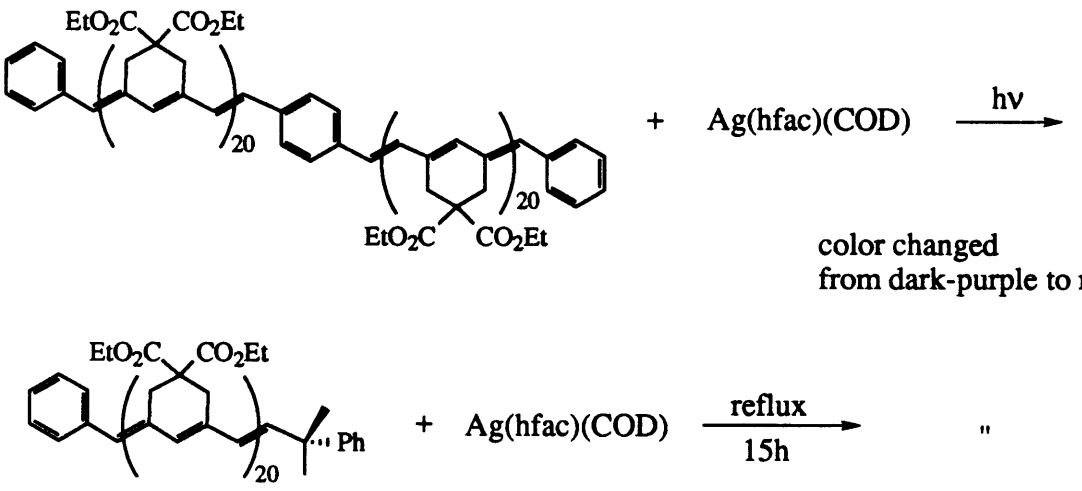
impossible. However, these heat treated polymers (2_n-Ag) were still soluble in THF and the UV spectrum of 2_{200}-Ag showed an absorption shift to 410 nm. The soluble 2_{200}-Ag was recast as a film and the recast polymer film of 2_{200}-Ag could be microtomed. It is probable that the brittleness resulted from a degradation of the film surface. The TEM micrograph of the recast film showed homogeneously dispersed Ag clusters (20 - 50 nm) (Figure 4.3). This result suggests that the silver clusters can be stabilized in polymer

Figure 4.3. TEM micrograph of recast polymer film of 2_{200}-Ag (——— = 2500 Å).

solution. Therefore, the generation of silver cluster in the polymer solution was tried.

$\mathbf{1_{200}}$ and Ag(hfac)(COD) were dissolved in toluene, stored in the dark for 24h to allow the complete coordination of the phosphine centers to the Ag(hfac)(COD), and then the mixture was heated at 100°C for 20h. A golden yellow turbid solution was generated and the UV spectrum of this solution was same as that of $\mathbf{2_{200}}$-**Ag**. It is unclear whether this blue shift of absorption of triblock copolymers containing silver cluster results from the coordination of polyene unit to the silver clusters or the decomposition of conjugated bonds during cluster formation. The decomposition of conjugated bonds is most likely, however, because of the reduction-oxidation charge balance. The reduction of silver complexes by heating to generate silver clusters needs something to be oxidized. Polyene block is easily oxidized and then degraded to give chain with a short conjugation length. The result of the substituted cyclopolyene doped with nanoclusters (CdSe) supports this explanation, where no UV absorption shift is detected (see next section).

Similar degradation of conjugated bonds was detected in thermal- or photo-chemical silver cluster formation reactions from the mixture of cyclopolyene and a precursor silver complex in THF (eq. 4.3). UV absorption bands were shifted to 400 nm in both cases.

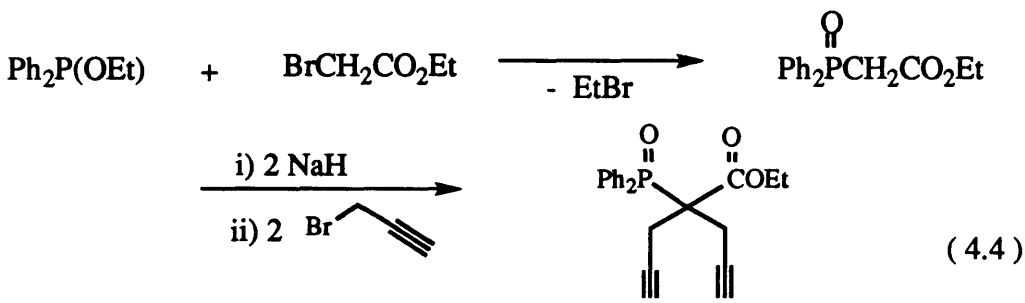


(4.3)

Polyenes with stabilized CdSe nanoclusters

Formation of metal clusters within a polyene structure through the reduction of the incorporated metal complexes often resulted in degradation of the conjugated polyene units, even under mild conditions (100°C). As a consequence, an alternative route was sought. A doping method of pre-formed stable nanoclusters into a polyene removes the possibility of degradation of the polyene unit. Recently CdSe nanocluster was synthesized by Moungi G. Bawendi's group from $CdMe_2$ and trioctylphosphinoselenium (TOPSe) in a high yield having a very narrow size distribution.[39] In addition, the clusters can be size-selectively separated by a simple precipitation method. CdSe clusters are stabilized by the coordination of trioctylphosphine and/or trioctylphosphine oxide and are very soluble in normal organic solvents with the exception of short-chain alcohols such as methanol. The cluster surface can be derivatized easily by adding an excess of a competing capping groups such as pyridine. Simply exchanging the stabilizing groups around the CdSe clusters with polymeric materials containing phosphine groups, e.g. polyNORPHOS, could lead to the desired materials.

A new diyne monomer (EPDPA, **3**) for cyclopolymerization having diphenylphosphine oxide group, need to coordinate the CdSe cluster surface, was prepared from ethyl diphenylphosphinite and ethyl bromoacetate (eq 4.4). A 25mer of EPDPA was



(4.4)

EPDPA (3)

prepared with a narrow polydispersity of 1.18 using $Mo(NAr)(CHCMe_2Ph)((OR_{F6})_2$ as the catalyst in DME solution. A UV spectrum showed a broad absorption with a maximum at 540 nm in THF. However, cast films with the CdSe cluster (12% by weight) were too brittle to microtome. A polyEPDPA 100mer was prepared in an analogous manner having a slightly broader polydispersity of 1.87. Films of the polyEPDPA 100mer with various amount of CdSe clusters were prepared by static casting from THF. TEM results of cast films are summarized in Table 4.2. When the

Table 4.2 CdSe cluster size in cast polyEPDPA films.

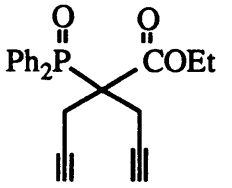
$(CdSe)_x$• n $P(O)Oct_3$ (wt%)	large chunk	small cluster
10%	1.5 μm	60 nm
4%	0.6 μm	60 nm
2%	0.2μm	60 nm
1%	no	30 nm

amount of CdSe cluster was higher than 1%, large chunks of CdSe and small nanoclusters (≈ 60 nm) were generated. With small amounts of CdSe clusters (1%), no more large chunks of CdSe were produced and only small clusters (30 nm) were formed. However the size of these clusters is much bigger than that of the original cluster (≈ 4.5 nm, λ_{max} = 580 nm)[39] and it is clear that aggregation of clusters occurs during the film casting. These preliminary results show that the coordinating ability of diphenylphosphonyl group in the cyclopolymer is sufficient to replace some of trioctylphosphine and/or trioctylphosphine oxide from the CdSe clusters surface but the stabilizing power is not high enough to prevent the aggregation of the clusters; probably due to the steric restriction of polymer chains. Recently, Dr. Rusty Blanski has checked the incorporation of CdSe clusters into $poly(MTD)_x(NORPHOS)_y$ (x = 300, y = 20 and 40) in a similar

way and the result showed the maximum value of incorporation was 0.6% even when the amount of NORPHOS units was much higher than that of trioctylphosphine on the cluster surface. The excess clusters were recovered via precipitation into pentane after doping for 24h in THF solution. When he used another polymer prepared from a monomer which had a long alkyl chain between the norbornene site and phosphorous center, the maximum incorporation of CdSe clusters was increased up to 7.6%. Although there is yet no direct evidence of cluster size after incorporated into the polymer, the release of the steric restriction of phosphorous center by introducing long alkyl chain seems to increase the incorporation of clusters into the polymer.

Attempts to prepare a new monomer

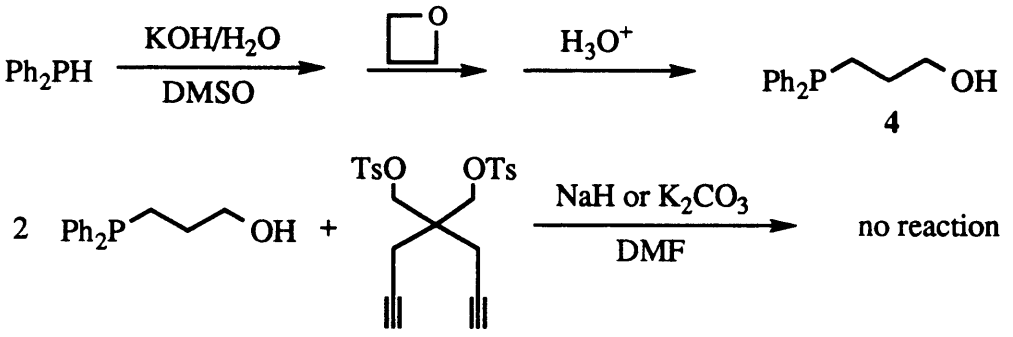
In order to increase the coordinating ability of the polymer to clusters, a reduction of phosphonyl group in EPDPA was tried with $HSiCl_3$ but only the starting material was recovered after being refluxed with $HSiCl_3$ in toluene for 40h (eq 4.5). This method was



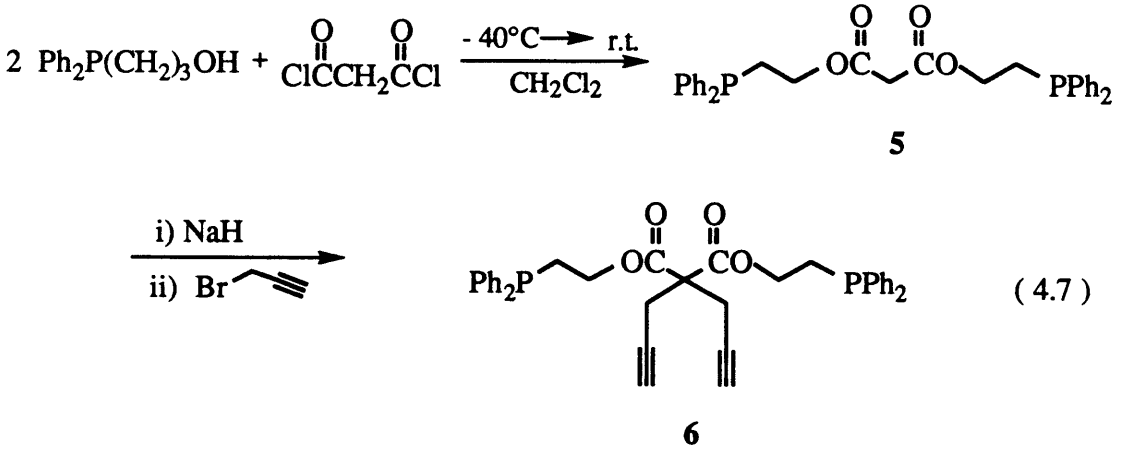
3

$$\xrightarrow[\text{toluene}\ 100°C,\ 40h]{HSiCl_3 \text{ or } HSiCl_3/Et_3N} \text{no reaction} \qquad (4.5)$$

previously used for the reduction of NORPHOS-O_2 to NORPHOS.[40] 3-Diphenylphosphinopropanol (**4**) was prepared from diphenylphosphine and trimethylene oxide in a high yield as a waxy solid (eq 4.6). However the subsequent coupling reaction with 4,4-bis(tosylmethyl)1,6-heptadiyne[20] failed. Another new monomer (**6**) was prepared from **4** and maleic dichloride in a similar way as the preparation of **3** (eq 4.7). However the monomer could not be sufficiently purified.



(4.6)



(4.7)

CONCLUSIONS

Triblock copolymers containing polyene block and metal precursor block were prepared by a living ROMP method using $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ as an initiator. Films prepared by static cast method showed lamella morphology when metal precursor block had a weight percentage higher than 40%. The mild heat treatment (at 150°C for 13h) of these triblock copolymers produced silver nanoclusters (5 - 10 nm) which resided in the microdomain where the precursor complexes originated. During the cluster formation, however, the degradation of the polyene block occurred, resulting in a shorter conjugation length of the polyene backbone, as observed by a shorter UV

absorption at 410 nm. This degradation is probably due to the oxidation of the polyene during cluster formation. Surface-stabilized CdSe nanocluster could be doped into a substituted cyclopolyene to produce homogeneously dispersed CdSe clusters in a polymer matrix. Clusters were highly aggregated when the amount of doped clusters was higher than 1%, probably due to the weak coordinating ability of diphenylphosphonyl groups in cyclopolyene and/or the steric restriction of polymer backbone. Future studies of polyenes with nanoclusters should be pursued for preparing modified monomers which have sterically less demanding phosphine centers and have a flexible long-chain linkage between the phosphine center and the polymer backbone.

EXPERIMENTAL PROCEDURES

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade THF and DME were vacuum transferred twice from sodium benzophenone ketyl. Polymerization grade toluene was stored over sodium / potassium alloy and passed through alumina prior to use.

HPLC grade solvents were used in Gel permeation chromatography (GPC) runs and were degassed prior to use. GPC was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Viscotek Differential Refractometer / Viscometer H-500, and a Spectroflow 757 absorbance detector on a samples 0.1 - 0.3% (w/v) in THF which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 - 2.75 x 10^6. NMR data were obtained at 300 MHz and listed in parts per million downfield from tetramethylsilane. Spectra were obtained at 25°C unless otherwise noted. Transmission

electron micrographs were taken in the bright-field mode on a JEOL 200CX instrument operating at 200 kV accelerating voltage.

All chemicals used were reagent grade and were purified by standard methods. $Mo(NAr)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$,[41] racemic 2-exo-3-endo-bis(diphenylphosphino)-bicyclo[2.2.1]heptene (NORPHOS),[40] 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (Feast)[42], Ag(hfac)(COD),[43] diethyl dipropargylmalonate (DEDPM),[20] $(CdSe)_x$ • n $POct_3$[39] were prepared as described in the literature. Methyltricyclododecene (MTD) was generously supplied from Goodrich and purified by the distillation over Na. Benzaldehyde from Aldrich was distilled over Na and stored at -35°C. Silica gel (70 - 230 mesh, 60Å) was used as received from Aldrich.

Triblock copolymers ($(MTD)_x(Feast)_{20}(NORPHOS)_{20}$). The preparation of the polymer in which x = 100 is provided as an example. MTD (159 mg, 910 μmol), Feast monomer (48 mg, 180 μmol) and NORPHOS (84 mg, 180 μmol) were polymerized successively with $Mo(NAr)(CHMe_2Ph)(O\text{-}t\text{-}Bu)_2$ (5.0 mg, 9.1 μmol) initiator in toluene for 10 min, 1h and 2h, respectively. Polymers were capped with excess benzaldehyde (9.3 μL, 91 μmol, 10 fold excess) for 1h, precipitated into pentane and dried in vacuum to afford yellow powdery polymer (0.28 g, 97%). Other polymers were prepared in a similar way. These polymers were stable at -40°C and could be kept for long period of time without a significant amount of retro Diels-Alder reaction.

Cast polymer film with Ag(hfac)(COD). The casting of $(MTD)_{100}(Feast)_{20}$-$(NORPHOS)_{20}$ with Ag(hfac)(COD) (1 equiv to the amount of diphenylphosphonyl group in the polymer) is shown as an example. Triblock copolymer (80 mg, 2.5 μmol) was dissolved in 3 mL of benzene (≈ 3% of polymer solution) with Ag(hfac)(COD) (42 mg, 100 μmol), and the solution was transferred into a small aluminum pan and allowed to evaporate slowly in the dark for 7 day. The dark-red flexible thin (≈ 0.4 mm) polymer films were obtained.

Ethyl (diphenylphosphonyl)acetate. $Ph_2P(OEt)$ (2.5 g, 11 mmol) was added to the ethyl bromoacetate (2.0 g, 12 mmol) solution in THF. EtBr was generated. After the mixture was stirred for 1h, solvent and excess ethyl diphenylphosphinite were removed in vacuo to give 3.1 g (99%) of white solid. ^1H NMR (C_6D_6) δ 7.70 (m, 4, ring proton), 7.02 (m, 6, ring proton), 3.75 (q, 2, OCH_2), 3.20 (d, 2, PCH_2O), 0.72 (t, 3, CH_3).

Ethyl dipropargyl(diphenylphosphonyl)acetate (EPDPA, 3). $Ph_2P(O)CH_2$-CO_2Et (3.1 g, 11 mmol) was added to the suspension of NaH (0.71 g of 80%, 24 mmol) in 20 mL of THF and the mixture was stirred for 30 min until H_2 bubbling stopped. A solution of propargyl bromide (2.6 g, 22 mmol) in 10 mL of THF was added to the mixture. The mixture was stirred for 20h, the salts were filtered and solvent was removed in vacuum. Recrystallization of crude product from THF/pentane gave 1.9 g (49%) of pure product: ^1H NMR ($CDCl_3$) δ 8.05-7.45 (m, 10, ring proton), 3.80 (q, 4, $-CH_2CH_3$), 3.1 (m, 4, $-CH_2-$), 1.93 t, 2, CH), 0.89 (t, 6, $-CH_3$).

Polymerization of EPDPA(3). The preparation of 25mer is shown as an example. A solution of $Mo(CHCMe_2Ph)(OR_{F6})_2$ (10 mg, 13 μmol) in 1.0 mL of DME was added to a solution of EPDPA (120 mg, 330 μmol) in 4 mL of DME . The mixture was stirred for 3h at 23°C and capped with benzaldehyde (6.5 μL, 62 μmol) for 15h. Polymer was precipitated into the pentane as a purple solid, filtered and dried in vacuo (118 mg, 98%, PDI = 1.18 in THF versus polystyrene standards). λ_{max} = 540 nm in THF. EPDPA 100mer was prepared in an analogous manner.

Cast polyEPDPA film with CdSe clusters. PolyEPDPA 100mer (50 mg) was dissolved in 2 mL of THF with an appropriate amount of stabilized CdSe cluster (1 mg, for 1% doped polymer). The mixture was transferred into a small aluminum pan and allowed to evaporate slowly for 2-3 days in the drybox.

$Ph_2P(CH_2)_3OH$ (4). A solution of KOH (1.8 g, 32 mmol) in 1.5 mL of water was added to a stirred solution of Ph_2PH (5.0 g, 27 mmol) in 10 mL of dried DMSO for 10 min to generate $Ph_2P^-K^+$. To this solution was added trimethylene oxide (3.12 g, 53.7

mmol, 2 folds excess) and the mixture was heated at 90°C for 1h. After the mixture was worked up with water, the product was extracted into ether. The extract was dried over $MgSO_4$ and solvent was removed in vacuo to give the desired product (5.95 g, 91%): ^1H NMR ($CDCl_3$) δ 7.55-7.24 (m, 10, ring proton), 3.68 (t, 2, -OC*H*$_2$-), 2.13 (t, 2, -PC*H*$_2$-), 1.85 (broad, 1, -O*H*), 1.68 (m, 2, -C*H*$_2$-).

$[Ph_2P(CH_2)_3O_2C]_2CH_2$ (5). A pre-cooled (-40°C) solution of malonyl dichloride (0.85 g, 6.0 mmol) in 10 mL of CH_2Cl_2 was added to a cold solution of $Ph_2P(CH_2)_3$ OH (3.0 g, 12 mmol) in 60 mL of CH_2Cl_2 and the mixture was allowed to warm to room temperature. After the mixture was stirred for 20h, the mixture was worked up with 10% Na_2CO_3 solution and the product was extracted into $CHCl_3$. The extract was dried over $MgSO_4$ and solvent was removed in vacuo. The crude product was dissolved in ether and insoluble sticky material was separated. After ether was removed, pale yellow product (2.3 g, 69%) was obtained: ^1H NMR ($CDCl_3$) d 7.50-7.15 (m, 20, ring proton), 4.12 (t, 4, -OC*H*$_2$-), 3.25 (s, 2, -COC*H*$_2$CO-), 2.00 (m, 4, -C*H*$_2$P-), 1.68 (m, 4, -C*H*$_2$-).

$[(Ph_2P(CH_2)_3O_2C]_2C(CH_2CCH)_2$ (6). A solution of $[Ph_2P(CH_2)_3O_2C]_2CH_2$ (**5**, 0.58 g, 1.0 mmol) in 2 mL of THF was added to the suspension of NaH (60 mg, 2.5 mmol) in 3 mL of THF. When evolution of H_2 stopped, a solution of propargyl bromide (0.25 g, 2.1 mmol) in 1 mL of THF was added. H_2 bubbled again and white salt formed. The mixture was stirred for 6.5h and salt was filtered. Solvent was removed in vacuo to give red viscous oil. Further purification was failed due to the instability of the compound.

REFERENCES

(1) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690.

(2) Prasad, P. N. in "Nonlinear Optical and Electroactive Polymers"; P. N. Prasad and D. R. Ulrich, Ed.; Plenum Press: New York City, 1987; pp 41.

(3) Kobayashi, T.; Hattori, T.; Terasaki, A.; Kurokawa, K. in "Nonlinear Optical and Electroactive Polymers"; P. N. Prasad and D. R. Ulrich, Ed.; Plenum Press: New York City, 1987; pp 137.

(4) Zyss, J.; Chemla, D. S. in "Nonlinear Optical Properties of Organic Molecules and Crystals"; D. S. Chemla and J. Zyss, Ed.; Academic Press: Orlando, Florida, 1987; Vol. 1; pp 23.

(5) Lytel, R.; Lipscomb, G. F.; Thackara, J.; Altman, J.; Elizondo, P.; Stiller, M.; Sullivan, B. in "Nonlinear Optical and Electroactive Polymers"; P. N. Prasad and D. R. Ulrich, Ed.; Plenum Press: New York, 1987; pp 415.

(6) Zyss, J. "Molecular Nonlinear Optics: Materials, Physics, and Devices"; First ed.; Academic Press: Boston, 1994.

(7) Shirikawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Commun.* **1977**, 578.

(8) Naarmann, H. *Synth. Met.* **1987**, *17*, 223.

(9) Kajzar, F.; Etemad, S.; Baker, G. L.; Messier, J. *Solid State Commun.* **1987**, *63*, 1113.

(10) Drury, M. R. *Solid State Commun.* **1988**, *68*, 417.

(11) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Puccetti, G.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1993**, *115*, 860.

(12) Zamani-Khamiri, O.; Hameka, H. F. *J. Chem. Phys.* **1980**, *73*, 5693.

(13) Soos, Z. G.; Ramasesha, S. *J. Chem. Phys.* **1989**, *90*, 1067.

(14) Pierce, B. M. *J. Chem. Phys.* **1989**, *91*, 791.

(15) de Melo, C. P.; Silbey, R. J. *J. Chem. Phys.* **1988**, *88*, 2567.

(16) Chopra, P.; Carlacci, L.; King, H. F.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7120.

(17) Zhao, M. T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1988**, *89*, 5535.

(18) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91*, 2696.

(19) Fox, H. H.; Schrock, R. S. *Organometallics* **1992**, *11*, 2763.

(20) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

(21) Fox, H. H. Ph. D. Thesis, MIT, 1993.

(22) Ricard, D.; Roussignol, P.; Flytzanis, C. *Optics Lett.* **1985**, *10*, 511.

(23) Hache, F.; Ricard, P.; Flytzanis, C. *J. Opt. Soc. Am. B* **1986**, *3*, 1647.

(24) Hache, F.; Ricard, D.; Flytzanis, C.; Kreibig, U. *Appl. Phys. A* **1988**, *47*, 347.

(25) Haus, J. W.; Kalyaniwalla, N.; Inguva, R.; Bloemer, M.; Bowden, C. M. *J. Opt. Soc. Am. B* **1989**, *6*, 797.

(26) Andrews, M. P.; Kuzyk, M. G. *Poym. Prepr.* **1991**, *32*, 105.

(27) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 24.

(28) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *J. Am. Chem. Soc.* **1992**, *114*, 7295.

(29) Ng Cheong Chan, Y.; Craig, G. S. W.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 885.

(30) Ng Cheong Chan, Y.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1993**, *5*, 566.

(31) Sankaran, V.; Cummins, C. C.; Schrock, R. R.; Cohen, R. E.; Silbey, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 6858.

(32) Sankaran, V.; Yue, J.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J. *Chem. Mater.* **1993**, *5*, 1133.

(33) Cummins, C. C.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 27.

(34) Tassoni, R.; Schrock, R. R. *Chem. Mater.* **1994**, *6*, 744.

(35) Kuzyk, M. G.; Paek, U. C.; Andrews, M. P. *Mat. Res. Soc. Symp. Proc.* **1991**, *214*, 3.

(36) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424.

(37) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989.

(38) Craig, G. S. W. Ph.D. Thesis, M.I.T., 1993.

(39) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706.

(40) Brunner, H.; Pieronczyk, W. *Angew. Chem., Int, Ed. Engl.* **1979**, *18*, 620.

(41) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(42) Liu, R. S. H.; Krespan, C. G. *Inorg. Chem.* **1969**, *34*, 1271.

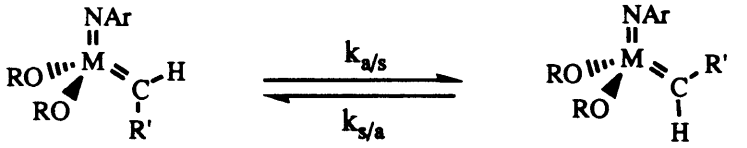
(43) Partenheimer, W.; Johnson, E. H. *Inorg. Synth.* **1976**, *16*, 117.

CHAPTER 5

The Role of Syn and Anti Alkylidene Rotamers of $Mo(NAr)(CHCMe_2Ph)(OR)_2$ in Determining ROMP Polymer Structure

INTRODUCTION

Alkylidene rotational isomers (rotamers, syn and anti) are found for many high-oxidation-state alkylidene complexes[1-4] (eq 5.1). However, rotamers are less often



anti syn (5.1)

$$K_{eq} = k_{a/s} / k_{s/a}$$

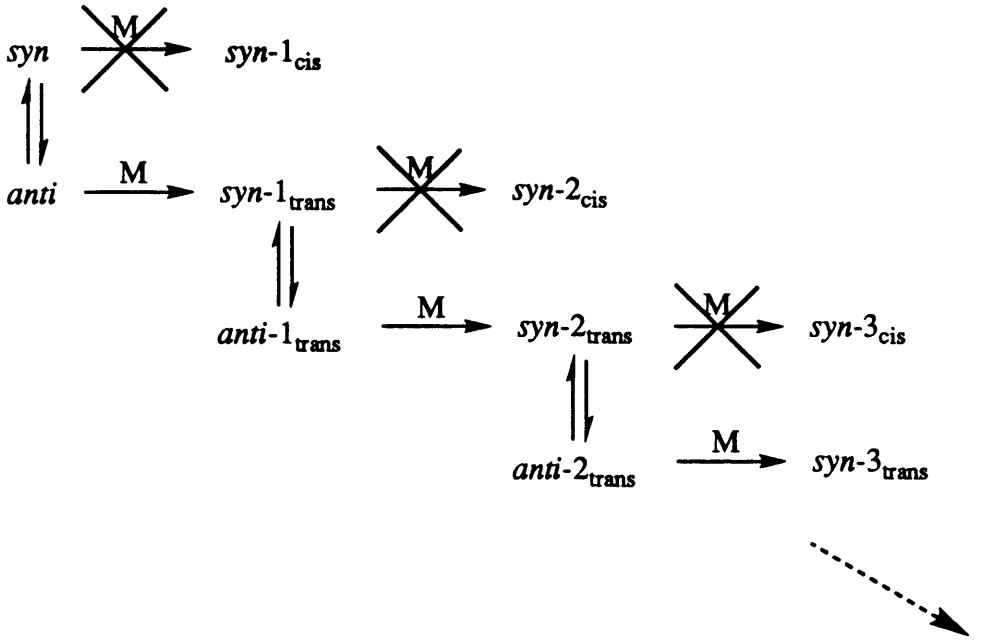
observed in four-coordinate complexes than five-coordinate base adducts and therefore the number of circumstances in which $k_{a/s}$ (or $k_{s/a}$) and K_{eq} can be measured is limited. For example, several molybdenum phenoxide alkylidene complexes consist of up to a 3 : 1 mixture of syn and anti rotamers at room temperature.[3,5] Rotamer interconversion was found to be first-order in metal and did not appear to proceed through a highly polar transition state. The barrier to rotamer interconversion ($\Delta G_{298}^{\ddagger}$) ranged from 15 to 18 kcal mol^{-1}. Recently, it was found that the ratio of rotamers could be altered by photolyzing the rotamer mixture and rate constants could be obtained by measuring the return of the mixture to equilibrium at various temperatures.[6-8] Energy barriers of 25 - 30 kcal mol^{-1} for Re(CR)(CHR)(OR')$_2$ and of 16 - 21 kcal mol^{-1} in toluene and 19 - 23 kcal mol^{-1} in THF for Mo(NAr)(CHR)(OR')$_2$ were determined for rotamer interconversion. The nature of the ligands dramatically changed the rate of rotamer interconversion. For example, syn and anti rotamers interconvert in t-butoxide complexes approximately five hundred times faster than in hexafluoro-t-butoxide complexes in Re complexes,[6] and six orders of magnitude faster in Mo complexes.[8] Theoretical studies support the experimental values ($\Delta G_{298}^{\ddagger}$ (calcd) = ~ 20 kcal mol^{-1}).[9,10] Furthermore, bending of the imido ligand was found to be an important stabilizing feature in a rotamer

interconversion, lowering the activation energy by ~ 50%. Experimental results showed that the rate of rotamer interconversion was enhanced by approximately three orders of magnitude in *ortho*-substituted phenyl imido complexes such as Mo(N-2-t-Bu-C_6H_4)($CHCMe_3$)[$OCMe(CF_3)_2$].[8] A single bulky substituent in the ortho position is proposed to promote bending of the imido ligand and therefore lowering of the barrier to rotamer interconversion.

It has been shown that rotamers can play a significant role in determining the primary structure in ROMP catalyst system.[8,11] The cis / trans ratio in ROMP polymers depends upon the relative reactivity of the syn and anti rotamers, the inherent reactivity of the monomer, and the rotamer interconversion rate. The syn rotamer of a substituted-phenylimido catalysts react with monomer to generate a first insertion product (syn-1_{cis}) having a cis double bond, while the anti rotamer reacts to give a first insertion product (syn-1_{trans}) having a trans double bond. For example, all-trans poly(2,3-bis-(trifluoromethyl)norbornadiene) (polyNBDF6)[2] prepared from Mo(N-2,6-i-Pr_2-C_6H_3)-($CHCMe_2Ph$)(O-t-Bu)$_2$ is proposed to arise from reactions involving only anti rotamers (normally unobservable) of chain propagating intermediates because the reactivity of the syn rotamer is so low that the anti rotamer is produced by isomerization of the syn rotamer to the anti rotamer and reacts (Scheme 5.1). Therefore anti must be much more reactive than syn, perhaps as much as 10^4 or 10^5.[8] On the other hand, when the syn rotamer is reactive and the rotamer interconversion rate is slow compared to the propagation rate, the syn rotamer reacts to generate all-cis polymers. For example, use of Mo(NAr)($CHCMe_2Ph$)[$OCMe(CF_3)_2$]$_2$ as the initiator yields all-cis polyNBDF6[12] (Scheme 5.2).

In this chapter several molybdenum phenoxide ROMP initiators were investigated in order to better understand the correlation between the reactivity of rotamers and the polymer structure (cis / trans ratio). The unique properties of phenoxide complexes, in which both rotamers are often observed at room temperature, and 2-t-butylphenylimido

complexes, which showed very fast rotamer interconversion,[8] are combined in one complex system. The most important finding is that the cis / trans structure of polymer is found to be temperature dependent in a manner that is consistent with the proposals by Dr John H. Oskam concerning the origin of cis and trans double bonds.[13]

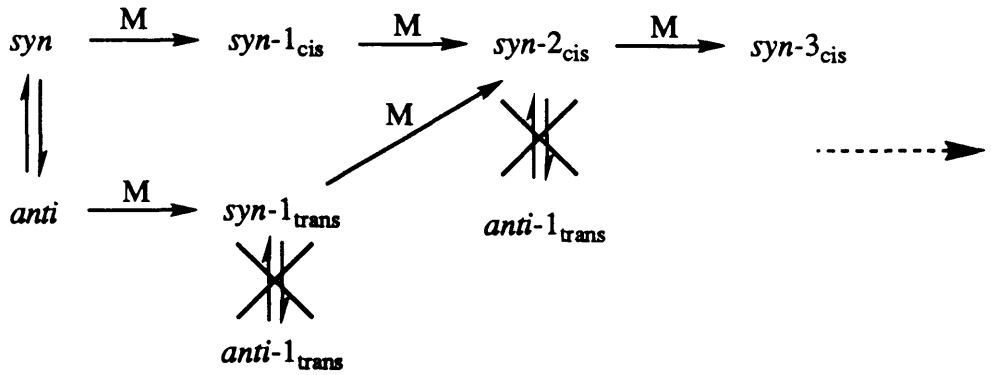


- For monomer M, reactivity of syn ≈ 0
  reactivity of syn << reactivity of anti
- Rotamer interconversion rate is fast relative to rate of formation of polymer

⇩

All trans polymer

Scheme 5.1. Proposed mechanism of formation of all-trans polymers.
The number refers to the number of monomers added whereas the subscript refers to the nature of that double bond prepared in the last step, e.g., syn-1_{cis} implies that the first insertion product is a syn alkylidene containing a cis double bond.



• For monomer M, reactivity of syn » 0
reactivity of syn « reactivity of anti

• During the polymerization, rotamer interconversion rate « propagating rate

⇩

All cis polymer

Scheme 5.2. Proposed mechanism of formation of all-cis polymer.

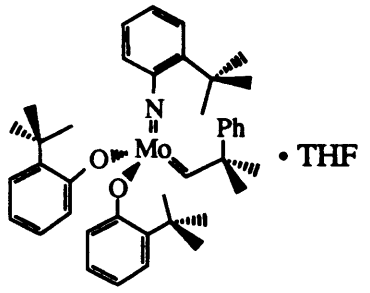
RESULTS AND DISCUSSION

Molybdenum 2-t-butylphenylimido neophylidene bisphenoxide complexes

Molybdenum 2-t-butylphenylimido neophylidene bisphenoxide complexes, Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)(OAr')$_2$ (OAr' = 2-t-Bu-C_6H_4O (**1**), 2,4-t-Bu$_2$-C_6H_3O (**2**)) and Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)(O_2Ar") (**3**) (O_2Ar" (Bipheno(t-Bu)$_4$) = 2,2'-[4,4',6,6'-(t-Bu)$_4$](C_6H_2)$_2O_2$) were prepared as a THF adduct from Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)(OTf)$_2$(DME) and the appropriate aromatic alkoxide such as LiOAr' or K$_2$(O_2Ar") (eq 5.2). ^{1}H NMR data for these complexes are summarized in Table 5.1

$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OTf)_2(DME) \quad + \quad 2\ LiOAr' \text{ or } K_2(O_2Ar'')$

THF | - 2 LiOTf or KOTf



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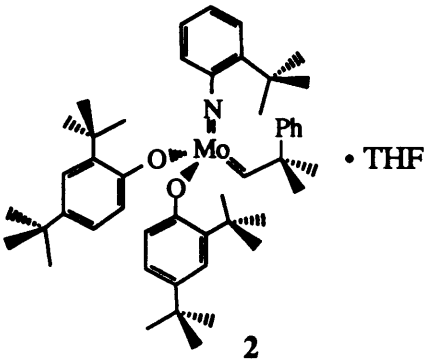

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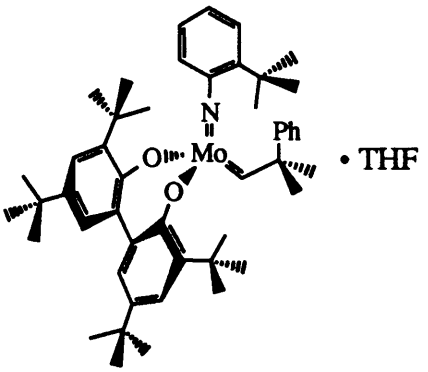
(5.2)



3

with other related complexes described later. Only **3** was a crystalline compound which could be easily purified to give a polymerization grade, pure catalyst. Only one broad alkylidene resonance was seen at 11.03 ppm for **3** (Figure 5.1). When the NMR sample of **3** was cooled, two new alkylidene resonances grew at 14.08 ppm and 12.85 ppm (Figure 5.1). These two alkylidene resonances sharpened at the expense of the 11.03 ppm resonance upon a further cooling of the sample to give finally a 1 : 3 ratio of two alkylidene resonances. Base-free $Mo(N\text{-}2\text{-}t\text{-}Bu\text{-}C_6H_4)(CHCMe_2Ph)(O_2Ar'')$ (**4**) could be prepared by removing THF in vacuo from a sample of **3** dissolved in a high boiling, non-

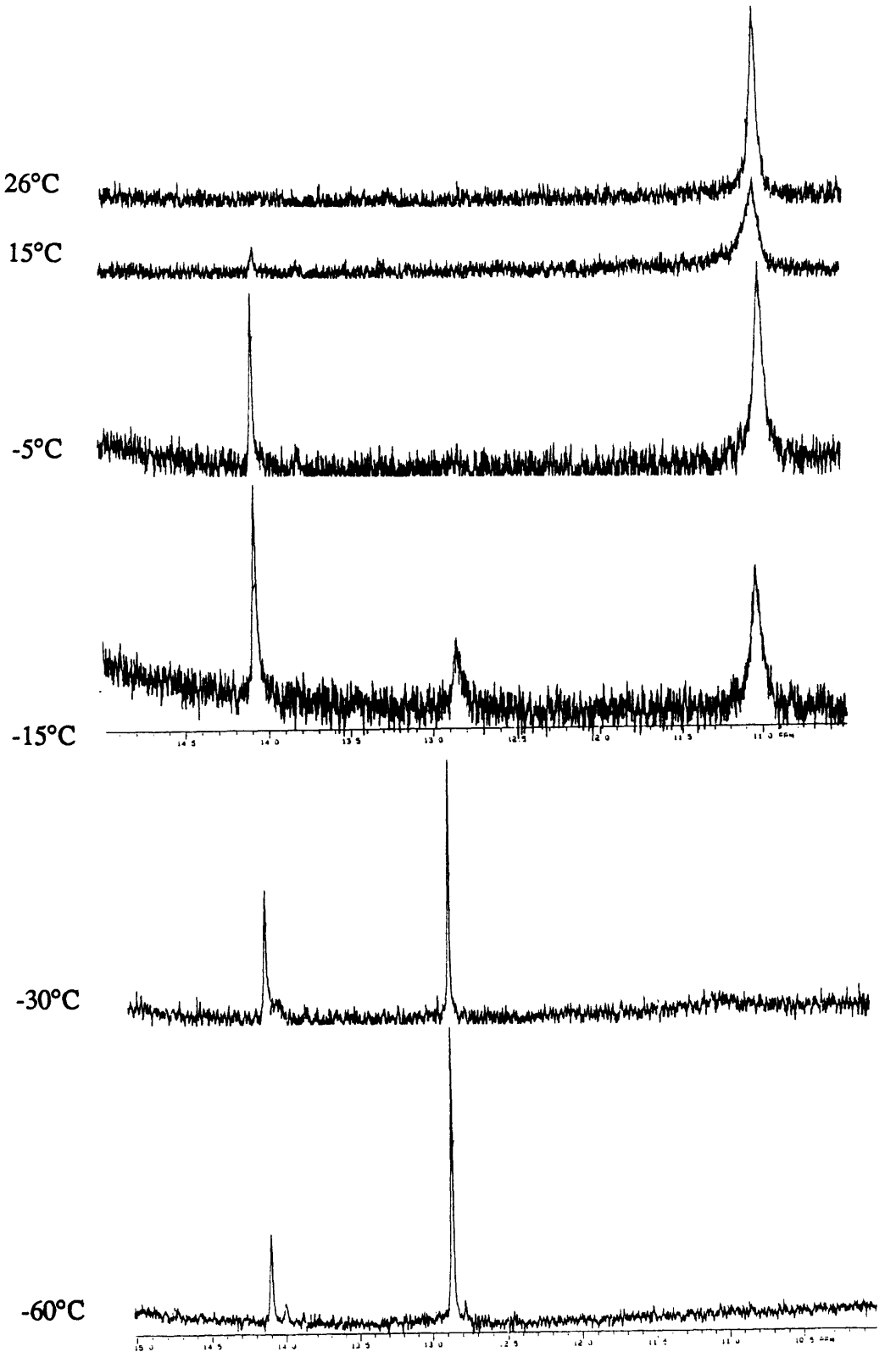


Figure 5.1. ^1H NMR spectra of **3** in alkylidene region at various temperatures (Toluene-d_8 solution).

coordinating solvent such as toluene. The ^{1}H NMR spectrum of **4** at 23°C showed one sharp alkylidene resonance at 10.87 ppm and no significant change was observed upon cooling the sample down to -65°C (Figure 5.2.a and b). Addition of THF (~ 10 equiv) at -65°C generated immediately two new alkylidene resonances, analogous to those formed from the THF adduct (**3**) at low temperature. This result implies that the resonances at 14.08 and 12.85 ppm are due to THF adducts of the syn and anti rotamers of **3**, i.e., $\mathbf{3}_{anti}$•THF and $\mathbf{3}_{syn}$•THF. The rate of rotamer interconversion at -65°C must be slow on the NMR time scale. As the temperature is raised, THF appears to come off the syn rotamer more rapidly than the anti rotamer, as judged by the spectra at -15°C and -5°C in Figure 5.1. Two unidentified tiny resonances at 12.78 and 14.00 ppm were observed near major resonances (Figures 5.1 and 5.2). They are assumed to be structural isomers in which THF coordinates to the metal in different positions. When this mixture was warmed, all the resonances coalesced into a broad resonance at 11.15 ppm as the equilibrium shifts toward the base-free form and THF exchange becomes rapid on the NMR time scale.

Photolysis of **4** was carried out in an attempt to produce $\mathbf{4}_{anti}$ at -75°C in toluene. However, no $\mathbf{4}_{anti}$ accumulated after 18h of photolysis, probably because the back reaction to give $\mathbf{4}_{syn}$ is fast on the chemical time scale. Bending of mono-substituted phenylimido ligand might reduce the energy barrier of rotation by stabilizing the intermediate state (or transition state), where the metal-carbon bond has rotated by 90° (Scheme 5.3).[9,10] If the energy barrier of rotation in complex **4** is small enough, $\mathbf{4}_{syn}$ and $\mathbf{4}_{anti}$ can reach equilibrium even at low temperature and no additional $\mathbf{4}_{anti}$ can build up.

Polymerization employing 3 or 4 as the initiator

Several polymerization reactions were carried out with **3** and **4** as the initiator. It can be assumed that $\mathbf{4}_{anti}$ is in equilibrium with $\mathbf{4}_{syn}$, and that trans and cis double bonds of polymer are formed from each, respectively, consistent with observations made

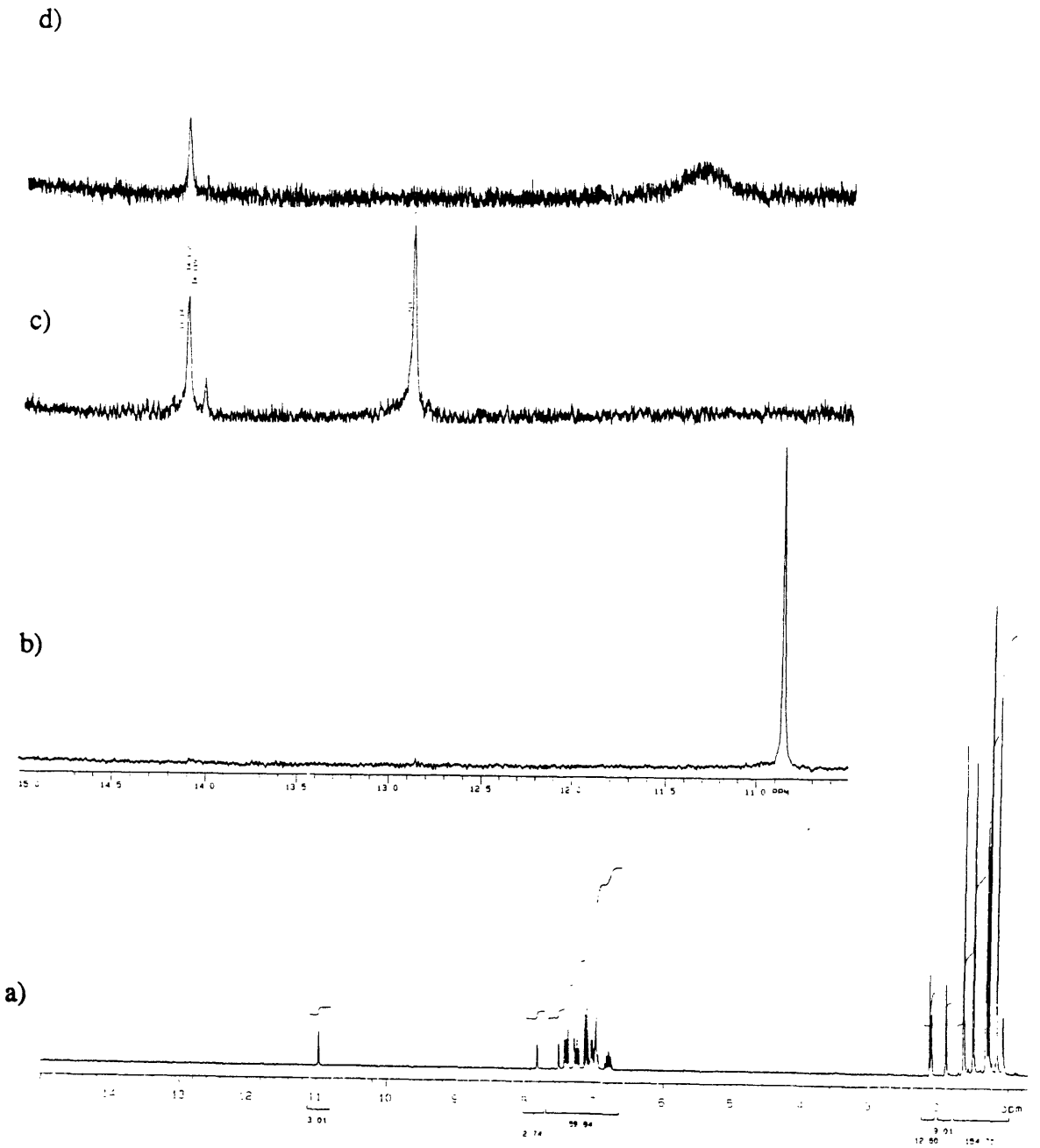
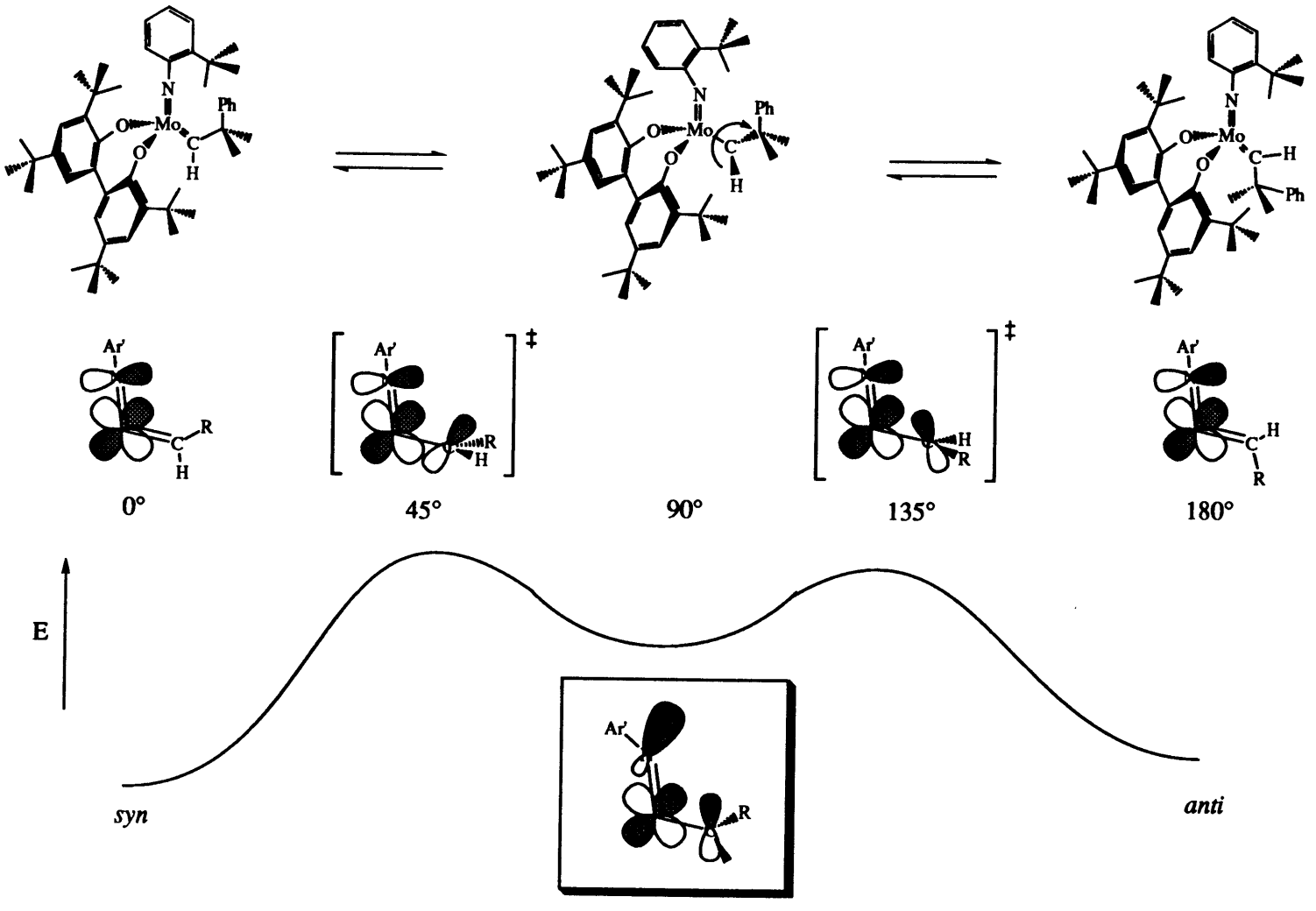


Figure 5.2. ^{1}H NMR spectra of **4** in Toluene-d_8.
(a) Whole spectrum at 23°C. (b) Alkylidene region at -65°C. (c) Alkylidene region at -65°C after addition of THF (~ 10 equiv). (d) Alkylidene region at 20°C after addition of THF (~ 10 equiv).



Scheme 5.3. Syn and anti interconversion pathway by metal-carbon bond rotation.

Table 5.1. Alkylidene ^1H chemical shift data of four- and five-coordinate Mo(VI) imido neophylidene bisalkoxide complexes.

Complex[a]	Base	$\delta(H_\alpha)$[b]	yield(%)
Mo(N-2-t-Bu-C_6H_4)(CHR)(O-2-t-Bu-C_6H_4)$_2$ (**1**)	THF	11.59[c] 13.14	oil
Mo(N-2-t-Bu-C_6H_4)(CHR)(O-2,4-t-Bu_2-C_6H_3)$_2$ (**2**)	THF	11.60	oil
Mo(N-2-t-Bu-C_6H_4)(CHR)[Bipheno(t-Bu)$_4$] (**3**)	THF	11.03	78
Mo(N-2-t-Bu-C_6H_4)(CHR)[Bipheno(t-Bu)$_4$] (**4**)	--	10.89	--
Mo(N-2-t-Bu-C_6H_4)(CHR)[$OCMe_2(CF_3)$]$_2$ (**5**)	--	11.28[d] 14.49	oil
Mo(N-2-t-Bu-C_6H_4)(CHR)[$OCMe(CF_3)_2$]$_2$ (**6**)	--	11.79	77[e]
Mo(N-2,6-Me_2-C_6H_3)(CHR)[Bipheno(t-Bu)$_4$] (**7**)	THF	11.52[f] 14.10	64[g]
Mo(N-2,6-i-Pr_2-C_6H_3)(CHR)(O-2-t-Bu-C_6H_4)$_2$ (**8**)	--	11.79[h] 13.37	91
Mo(N-2,6-i-Pr_2-C_6H_3)(CHR)(O-2,4-t-Bu_2-C_6H_3)$_2$ (**9**)	--	11.66[i] 13.19	oil
Mo(N-2,6-i-Pr_2-C_6H_3)(CHR)[Bipheno(t-Bu)$_4$] (**10**)	THF	11.43[j] 14.30	68
Mo(N-2,6-i-Pr_2-C_6H_3)(CHR)[$OCMe_2(CF_3)$]$_2$ (**11**)	--	11.68	53[e]
Mo(N-2,6-i-Pr_2-C_6H_3)(CHR)[$OCMe(CF_3)_2$]$_2$ (**12**)	--	12.12	86[k]

(a) R = CMe_2Ph (b) Values are reported in ppm in C_6D_6 at ~ 23°C (c) syn/anti = 10/1
(d) syn/anti = 2/1 (e) reference 19 (f) syn/anti = 7/1 (g) reference 13 (h) syn/anti = 14/1
(i) syn/anti = 14/1 (j) syn/anti = 3/1 (k) reference 20

Table 5.2. PolyNBDF6 100mers prepared employing **4** as the initiator.

T (°C)	solvent	time (h)	cis/trans[a]	PDI[b]	yield (%)
-35	THF	48	100/0	--	~5
-10	THF	48	100/0	--	~5
15	THF	24	83/17	1.38	43
23	THF	5	58/42	1.17	90
	toluene[c]	5	32/68	1.34	98
65	THF	5	24/76	1.10	99

(a) Measured by ^{1}H and ^{13}C NMR as described elsewhere.[14] (b) In THF versus polystyrene standards. (c) Immiscible material formed during polymerization. In THF, the reaction was homogeneous.

for t-butoxide and fluorinated t-butoxide complexes.[8] Poly(NBDF6)$_{100}$ synthesized employing **4** as the catalyst in THF or toluene is analyzed as shown in Table 5.2. Yields are low at low temperature as a consequence of the slow rate of reaction of adducts. It is assumed that only THF-free complexes are reactive. The polymers prepared at 23°C contained only 32% cis bonds. The small amount of cis compared to 72% and ≥ 98% cis bonds in polyNBDF6 prepared with **6**[8] and **12**,[12] respectively, is consistent with a greater accessibility of the anti rotamer as a consequence of faster rotamer interconversion. Evidence in support of this explanation can be obtained by changing the monomer. A more reactive monomer would be expected to give rise to a polymer having more cis double bond as a consequence of more propagation via the syn rotamer. In fact, poly(2,3-dicarbomethoxynorbornadiene) (polyDCMND) prepared with **4** in toluene at 23°C has 54% cis bonds compared to 32% for the less reactive NBDF6 monomer (Tables 5.2 and 5.3).

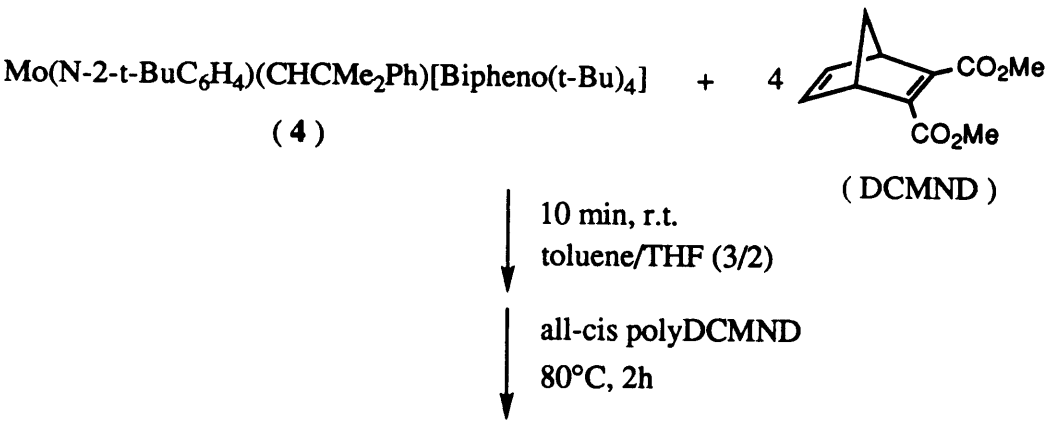
Table 5.3. PolyDCMND 100mers prepared employing **4** as the initiator.

T (°C)	solvent	time (h)	cis/trans[a]	yield (%)
-35	CH_2Cl_2[b]	12	100/0	36
23	toluene	1	54/46	93
50	toluene	1	35/65	96
80	toluene	1	19/81	93

(a) Measured as described elsewhere.[14] (b) Polymer was prepared in CH_2Cl_2 in order to enhance solubility at low temperature.

Polymerization at various temperatures was carried out in an attempt to see the temperature dependency of the polymer structure as a consequence of a change in K_{eq} of syn and anti rotamers. PolyNBDF6 and polyDCMND prepared at various temperatures showed a trend toward higher cis at low temperature as a consequence of a slowing of the rotamer interconversion rate relative to propagation via the syn rotamer; the yield, however, suffers accordingly. At higher temperatures, more anti is accessible and more trans bonds therefore are generated (Tables 5.2 and 5.3). A control experiment ruled out the possibility that secondary metathesis was responsible for formation of trans polymer at higher temperatures (eq 5.3). The all-cis polyDCMND[15] prepared using **7** as the catalyst was added to the living alkylidene solution generated from **4** and DCMND, and the mixture was heated for 2h at 80°C. No significant trans bonds were generated under this reaction condition. The other possibility that the addition of monomers to other than the C/N/O face of catalysts at high temperature, is unlikely based on the results of polymers prepared using **7** as the catalyst (Table 5.4). Polymers prepared employing **7** as the catalyst always have all-cis bonds.

A solvent effect was also found in polymerizations of NBDF6. Polymerization of NBDF6 in THF and in toluene generated 58% and 32% cis bonds, respectively (Table 5.2). The higher cis content of the polymer prepared in THF can be explained by the



(5.3)

no trans bonds were generated

Table 5.4. PolyDCMND and polyNBDF6 100mers prepared employing **7** as the initiator.

polymer	T (°C)	solvent	time (h)	cis/trans[a]	PDI[b]	yield (%)
DCMND	23	toluene	1	100/0	--	96
	23	CH_2Cl_2	1	100/0	--	96
	80	toluene	1	100/0	--	100
NBDF6	23	toluene	5	100/0	c	91
	23	THF	5	100/0	1.26	92

(a) Measured as described elsewhere.[14] (b) In THF versus polystyrene standards. (c) Very broad molecular weigh distribution.

preferential coordination of THF to the anti rotamer, which is known to have a greater affinity for bases (either σ-donor or π-donor) than the syn rotamer in other systems, as well as here (see above).[7,13] Coordination of THF attenuates the catalytic reactivity of anti rotamer and consequently more cis bonds are produced via syn rotamer intermediates.

The temperature dependency of the polymer structure

In order to confirm the syn and anti rotamer accessibility as the origin of the temperature dependency of the polymer structure, poly(NBDF6)$_{100}$ was prepared employing several catalysts (**6, 11** and **12**) at various temperatures.(Table 5.5). The nature of the first insertion products have been fully studied for **6, 11** and **12**.[8] . It is known that when these catalysts react with NBDF6, syn exclusively generates syn-1$_{cis}$ while anti generates syn-1$_{trans}$ (eq 5.4).[8] It has also been reported that both syn and anti

$$\text{syn-1}_{cis} \xleftarrow{\text{NBDF6}} \text{syn} \underset{k_{a/s}}{\overset{k_{s/a}}{\rightleftharpoons}} \text{anti} \xrightarrow{\text{NBDF6}} \text{syn-1}_{trans} \qquad (5.4)$$

rotamers are much more reactive in toluene than they are in THF and that the reactivity of an anti rotamer is decreased more significantly in THF than the reactivity of a syn rotamer in THF, relative to their reactivities in toluene.

In general, polymers prepared at higher temperatures have higher trans contents and polymers prepared in THF always have higher cis contents compared to those prepared in toluene. The change in the polymer structure (cis/trans ratio) with temperature is much greater with the 2-t-butylphenylimido catalyst (Tables 5.2 and 5.5) than with the 2,6-diisopropylphenylimido catalysts (Table 5.5). These results are consistent with the proposed polymerization mechanism (Scheme 5.1 and 5.2), i. e., anti rotamer accessibility via rotamer interconversion is the main factor that leads to higher trans polymer, and that THF reduces the reactivity of an anti rotamer more strongly to produce high cis content of the polymer compared to the polymer prepared in toluene. This solvent effect can be compared with the effect of adding a coordinating base to the polymerization reaction.[16-18]

Table 5.5. PolyNBDF6 100mers prepared at various temperatures.

T (°C)	solvent	time (h)	cis/trans[a]	PDI[b]	yield(%)
Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (**6**)					
-35	toluene	24	97/3	1.56[c]	83
23	toluene	5	78/22	1.18	100
	THF	5	87/13	--	21[d]
65	toluene	5	29/71	1.32[c]	97
Mo(N-2,6-i-Pr$_2$-C_6H_3)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ (**11**)					
-35	toluene	48	56/44	1.99	63[d]
23	toluene	5	36/64	1.24	100
65	toluene	5	9/91	1.61[c]	95
23	THF	5	50/50	1.32	50[d]
65	THF	5	13/87	1.34[c]	99
Mo(N-2,6-i-Pr$_2$-C_6H_3)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (**12**)					
25	toluene	5	97/3	1.28[c]	100
65	toluene	5	88/12	1.29[c]	94
23	THF	5	96/4	1.29	27[d]
65	THF	5	83/17	1.98	45[d]

(a) Measured as described elsewhere.[14] (b) In THF versus polystyrene standards. (c) Significant amount of double molecular weight peak was detected. The PDI value includes the double molecular weight peak. (d) Incomplete polymerization.

Two other 2,6-diisopropylphenylimido phenoxide catalysts (**8** and **10**) were used to make poly(NBDF6)$_{100}$ at various temperatures. The results, summarized in Table 5.6, are totally consistent with the trend toward higher trans content of the polymer at higher temperature and in toluene.

Table 5.6. PolyNBDF6 100mers prepared employing **8** and **10** as the initiator at various temperatures.

T (°C)	solvent	time (h)	cis/trans[a]	PDI[b]	yield (%)
Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(O-2-t-Bu-C$_6$H$_4$)$_2$ (**8**)					
-35	THF	50	78/22	--	23
23	THF	5	69/31	1.28	90
	toluene	5	65/35	1.82	92
65	THF	5	39/61	1.14	100
Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)[Bipheno(t-Bu)$_4$] (**10**)					
-35	THF	48	--	--	0
23	THF	5	99/1	1.33	98
65	THF	5	90/10	1.19	96

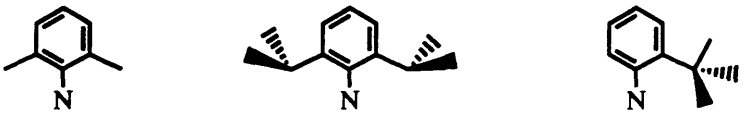
(a) Measured as described elsewhere.[14] (b) In THF versus polystyrene standards.

The determination of cis / trans polymer structure

As described in the introduction, the cis / trans polymer structure is proposed to depend upon the relative reactivity of the syn and anti rotamers, the inherent reactivity of monomer, and the rotamer interconversion rate. In this section, several selected polymers are compared to emphasize the relevancy of the proposed mechanism (two extreme cases are shown in Scheme 5.1 and 5.2).

In Table 5.7, the results of polyNBDF6 100mers prepared using different phenylimido catalysts which have the same alkoxide (Bipheno(t-Bu)$_4$) are summarized.

Table 5.7. Polymer structures prepared using [Bipheno(t-Bu)$_4$] catalysts with different imido ligands.



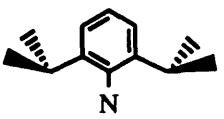
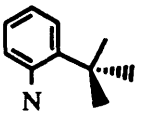
100/0[a] (100/0)[b]	99/1	58/42 (32/68)[b]

(a) Cis / trans ratio in polymer prepared in THF. (b) Prepared in toluene.

The unsymmetrically-substituted phenylimido (2-t-butylphenylimido) catalyst, which has a much faster rotamer interconversion rate, produces a high trans content (~ 50 %). This is predicted to be the case when the propagating rates of different catalysts are similar but their syn and anti rotamers interconversion rates are significantly different.

On the other hand, when the rotamer interconversion rates are similar but the propagating rates are different, a cis content of the polymer increases with the increment of the propagating rates of the polymerization (Table 5.8). The catalyst having the more electron-withdrawing alkoxide is more reactive. The relative electron-withdrawing abilities of alkoxides can be estimated from the acidity of the corresponding alcohols in aqueous solution.[19] Several pK_a values of some relevant alcohols are summarized in Table 5.9.

Table 5.8. Polymer structures prepared using N-2-t-Bu-C_6H_4 and N-2,6-i-Pr_2-C_6H_3 alkylidene catalysts with different alkoxide ligands.

		
$OCMe_3$	100/0[a] (100/0)[b]	--
$OCMe_2(CF_3)$	50/50 (36/64)[b]	--
Bipheno(t-Bu)$_4$	99/1	58/42 (32/68)[b]
$OCMe(CF_3)_2$	96/4 (97/3)[b]	87/13 (78/22)[b]
$O(CF_3)_3$	--	(99/1)[b,c]

(a) Cis / trans ratio in polymer prepared in THF. (b) Prepared in toluene. (c) Reference 8.

Table 5.9. pK_a values[19] of relevant alcohols in aqueous solution.

alcohol	pK_a
2-t-Bu-C_6H_4OH	10.6
2,4-t-Bu_2-C_6H_3OH	11.7
Me_3COH	19.2
$(CF_3)_2MeCOH$	9.6
$(CF_3)_3COH$	5.4

CONCLUSIONS

New molybdenum neophylidene complexes which contain unsymmetrically-substituted phenylimido ligand as well as phenoxide ligands were prepared. Variable temperature NMR experiments and photolysis of these complexes showed a very fast rotamer interconversion even at low temperatures. Consistent with this result, polymers prepared employing these complexes as a catalyst contain a high content of trans bonds compared to polymers prepared using other catalysts which have the same alkoxide ligands. The temperature dependency of the polymer structure was observed in an unsymmetrically-substituted phenylimido catalyst system. The temperature dependency of the polymer structure was also observed in all the other catalyst systems, although it is small in symmetrically-substituted phenylimido catalyst systems. The polymer structure also depended upon the solvent that was used for the polymerization. The reactivity of both syn and anti rotamers are attenuated by the coordination of THF, and the reactivity of an anti rotamer is decreased more strongly in THF than that of a syn rotamer in THF relative to their reactivities in toluene as has been previously observed.[8] As a result, many incomplete polymerizations were observed in THF at low temperature and the resulted polymers had a high cis content of the polymer compared to the polymer prepared in toluene.

The correlation between the accessibility of an anti rotamer in alkylidene catalysts and the polymer structure, is consistent with the proposed polymerization mechanisms (Scheme 5.1 and 5.2). First, the faster the rotamer interconversion rate, the higher is the trans content of the polymer. Second, the faster the propagation rate (the higher the reactivity of catalyst, or the higher the reactivity of the monomer), the higher is the cis content of the polymer.

EXPERIMENTAL PROCEDURES

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade THF was vacuum transferred twice from sodium benzophenone ketyl. Polymerization grade toluene was stored over sodium / potassium alloy and passed through alumina prior to use.

HPLC grade solvents were used in Gel permeation chromatography (GPC) runs and were degassed prior to use. GPC was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Viscotek Differential Refractometer / Viscometer H-500, and a Spectroflow 757 absorbance detector on a samples 0.1 - 0.3% (w/v) in THF which were filtered through a Millex-SR 0.5 μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1260 - 2.75 x 10^6. NMR data were obtained at 300 MHz and listed in parts per million downfield from tetramethylsilane. Spectra were obtained at 25°C unless otherwise noted. Elemental analysis (C, H, N) was performed on a Perkin-Elmer 2400 CHN analyzer.

All the chemicals used were reagent grade and purified by standard methods. Benzaldehyde was purchased from Aldrich, and was distilled over Na and pass over alumina before use. 2,2-[1-(OH)-4,6-t-Bu_2-C_6H_2]$_2$ (Biphenol-(t-Bu)$_4$), Mo(N-2-t-Bu-C_6H_4)(CHCMe_2Ph)(OTf)$_2$(DME)[20], Mo(N-2-t-BuC_6H_4)(CHCMe_2Ph)[OCMe(CF_3)$_2$]$_2$[20] (**6**), Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)[Bipheno(t-Bu)$_4$][15] (**7**), Mo(N-2,6-i-Pr_2-C_6H_3)(CHCMe_2Ph)(O-2-t-Bu-C_6H_4)$_2$[5] (**8**), Mo(N-2,6-i-Pr_2-C_6H_3)(CHCMe_2Ph)-[OCMe_2(CF_3)]$_2$[20] (**11**), and Mo(N-2,6-i-Pr_2-C_6H_4)(CHCMe_2Ph)[OCMe(CF_3)$_2$]$_2$[21] (**12**) were prepared as described in the literature.

The synthesis of molybdenum substituted-phenylimido neophylidene alkoxide complexes followed the reported procedure.[5] The experimental details of the synthesis of

1 is shown below as an example.

Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)(O-2-t-Bu-C_6H_4)$_2$(THF) (1). Li(O-2-t-Bu-C_6H_4) (204 mg, 1.31 mmol), prepared from 2-t-butylphenol and n-BuLi, was added as a solid to the pre-cooled solution of Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)(OTf)$_2$(DME) (500 mg, 0.65 mmol) in 50 mL of THF. The mixture was stirred for 3h and the color changed from yellow to orange-red. After solvent was removed in vacuo, the product was extracted into pentane and the insoluble lithium salts were removed by filtration. Solvent was removed from the filterate in vacuo to give the product (0.41 g, 93%) as a dark-yellow oil. Crystals were observed to form at -40°C in pentane but isolation failed due to melting of the product (~ 20°C): ^{1}H NMR (C_6D_6) δ 13.14 (s, anti H_α), 11.59 (s, 1, syn H_α), 7.50-6.75 (m, 17, H_{aryl}), 3.59 (br s, 4, OCH_2CH$_2$), 1.75 (s, 6, CH_3), 1.56 (s, 18, CMe_3), 1.39 (s, 9, CMe_3); (C_6D_6, 70°C) δ 11.64 (br s, 1, H_α).

Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)(O-2,4-t-Bu$_2$-C_6H_3)$_2$(THF) (2). ^{1}H NMR (C_6D_6) δ 11.60 (s, 1, H_α), 7.50-6.78 (m, 15, H_{aryl}), 3.60 (br s, 4, OCH_2CH$_2$), 1.78 (s, 6, CH_3), 1.62 (s, 18, CMe_3), 1.40 (s, 9, CMe_3), 1.30 (s, 18, CMe_3).

Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)[Bipheno(t-Bu)$_4$](THF) (3). ^{1}H NMR (Toluene-d_8) δ 11.03 (br s, 1, H_α), 7.80-6.70 (m, 13, H_{aryl}), 3.55 (m, 4, OCH_2CH$_2$), 1.86 (s, 3, CH_3), 1.61 (s, 9, CMe_3), 1.47 (s, 9, CMe_3), 1.44 (m, 4, OCH$_2$CH_2), 1.31 (s, 9, CMe_3), 1.28 (s, 9, CMe_3), 1.24 (s, 3, CH_3), 1.17 (s, 9, CMe_3); (Toluene-d_8, -60°C) δ 14.08 (s, anti H_α), 12.85 (s, syn H_α); ^{13}C NMR (Toluene-d_8, -60°C) δ 311.2 (*C*HCMe$_2$Ph, anti), 299.5 (*C*HCMe$_2$Ph, syn), other resonances were obscured.

Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)[Bipheno(t-Bu)$_4$] (4). The THF-free complex (**4**) was obtained quantitatively as a dark-red powder by dissolving **3** in toluene and removing all solvent in vacuo: ^{1}H NMR (Toluene-d_8) δ 10.87 (s, 1, H_α), 7.80-6.75 (m, 13, H_{aryl}), 1.87 (s, 3, CH_3), 1.61 (s, 9, CMe_3), 1.47 (s, 9, CMe_3), 1.30 (s, 9, CMe_3), 1.28 (s, 9, CMe_3), 1.17 (s, 9, CMe_3), 1.14 (s, 3, CH_3); ^{13}C NMR (Toluene-d_8) δ 279.9 (d, $^1J_{CH}$ = 120, CHCMe$_2$Ph), 156.7, 155.9, 153.0, 151.9, 144.8, 144.7, 141.7, 141.6, 132.9, 132.3,

129.7, 128.9, 128.8, 127.3, 126.7, 126.6, 126.5, 126.3, 126.0 (C_{aryl}), 55.2 (CMe_2Ph), 37.0 (CMe_3), 36.6 (C*Me*MePh), 35.8 (CMe*Me*Ph), 35.2 (CMe_3), 35.1 (CMe_3), 33.3 (CMe_3), 32.1 (C*Me*$_3$), 32.0 (CMe_3), 31.9 (C*Me*$_3$), 31.0 (C*Me*$_3$), 30.4 (C*Me*$_3$). Anal. Calcd for $C_{48}H_{65}NO_2Mo$: C, 73.54; H, 8.36; N, 1.79. Found: C, 73.87; H, 8.18; N, 1.51.

Mo(N-2-t-Bu-C_6H_4)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$ (5). ^{1}H NMR (C_6D_6) δ 14.50 (s, anti H_α), 11.19 (s, 1, syn H_α), 7.25-6.90 (m, 9, H_{aryl}), 3.60 (m, 4, OC*H*$_2$CH$_2$), 1.53 (s, 6, C*H*$_3$), 1.40-1.33 (br s, 13, OCH$_2$C*H*$_2$ and C*Me*$_3$), 1.13 (s, 3, OC*Me*Me(CF$_3$)), 1.11 (s, 3, OCMe*Me*(CF$_3$)).

Mo(N-2,6-i-Pr$_2$-C_6H_3)(CHCMe$_2$Ph)(O-2,4-t-Bu$_2$-C_6H_3)$_2$ (9). ^{1}H NMR (C_6D_6) δ 13.19 (s, anti H_α), 11.66 (s, 1, syn H_α), 7.55-6.60 (m, 14, H_{aryl}), 3.70 (sept, 2, C*H*Me$_2$), 1.74 (s, 3, C*H*$_3$), 1.60 (s, 18, C*Me*$_3$), 1.31 (s, 18, C*Me*$_3$), 1.30 (s, 3, C*H*$_3$), 1.04 (d, 6, CH*Me*$_2$).

Mo(N-2,6-i-Pr$_2$-C_6H_3)(CHCMe$_2$Ph)[Bipheno(t-Bu)$_4$](THF) (10). ^{1}H NMR (C_6D_6) δ 14.06 (s, anti H_α), 11.46 (s, 1, syn H_α), 7.80-6.90 (m, 12, H_{aryl}), 3.81 (sept, 2, C*H*Me$_2$), 3.52 (br s, 2, OC*H*$_2$CH$_2$), 1.90 (s, 3, C*H*$_3$), 1.60 (d, 6, CH*Me*$_2$), 1.55 (s, 18, C*Me*$_3$), 1.42 (s, 3, C*H*$_3$), 1.29 (br s, 13, C*Me*$_3$and OCH$_2$C*H*$_2$), 1.20 (s, 9, C*Me*$_3$), 0.96 (d, 6, CH*Me*$_2$). Anal. Calcd for $C_{54}H_{77}NO_3Mo$: C, 73.36; H, 8.78; N, 1.58. Found: C, 73.23; H, 9.49; N, 1.43.

Polymerization reactions. The following is a typical procedure. A solution of NBDF6 (310 mg, 1.36 mmol) in 4 mL of toluene was added to a solution of **6** (10.0 mg, 13.6 μmol) in 1 mL of toluene heated to 65°C in the oil bath. The mixture was stirred for 5h at 65°C and benzaldehyde (14.0 μL, 134 μmol) was added to terminate the reaction. The mixture was stirred for 1h and the polymer was precipitated in methanol and dried in vacuo to give 300 mg (97%). For polymerizations at low temperature, a pre-cooled (-35°C) solution containing the monomer was added to the cold catalyst solution and the mixture was kept at approximately -35°C in the drybox freezer. The mixture was stirred several times during the polymerization reaction.

REFERENCES

(1) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(2) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

(3) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

(4) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

(5) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(6) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 3367.

(7) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

(8) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

(9) Cundari, T. R.; Gordon, M. S. *Organometallics* **1992**, *11*, 55.

(10) Fox, H. H.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1994**, *13*, 2804.

(11) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1399.

(12) Feast, W. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.

(13) Oskam, J. H. Ph. D. Thesis, M.I.T., 1993.

(14) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.

(15) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.

(16) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

(17) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004.

(18) Wu, Z.; Wheeler, D. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 146.

(19) "Ionization Constants of Organic Acids in Aqueous Solution"; Pergamon: New York, 1979.

(20) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organometal. Chem.* **1993**, *459*, 185.

(21) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

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